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EFFECT OF HORNIFICATION ON THE PROPERTIES OF THERMALLY MODIFIED SCOTS PINE UNDER SATURATED STEAM

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 13 February, 2017.

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Abstract of master's thesis

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Abstract

The aim of this thesis was to investigate the effect of hornification on the properties of Scots pine thermally modified under saturated steam. Experiment was carried out to never-dried Scots pine samples at temperatures of 160 °C and 170 °C under saturated steam for 3 hours. After the modification, samples were dried at 75 °C at five different RH: 0%, 25%, 50%, 75% and 95%. EMC at 20 °C and RH 65%, impact strength, MOE and MOR, swelling and ASE were then tested and compared. Addition to those, hornification was measured using deuterium exchange method in DVS apparatus. The method for DVS was developed, and resulted to the adding of re-wetting step to the process and using of 12 hours impregnation time for deuterium oxide. Finally, HPAEC and GC-MS were used to analyse condensation water and the acetone soluble compounds from modified and unmodified samples.

Based on the results, EMC differed at 160 °C treatment but not at 170 °C treatment. Accessibility of hydroxyl groups was measured with DVS from the 160 °C samples dried at 50% and 95%, and was found to have significant differences. Therefore, it was concluded that a difference in hornification is possible due to the initial drying. Mechanical tests and swelling test had no statistical difference between the different assumed states of hornification in this experiment. Chemical analysis revealed that condensation water contained many sugars from hemicelluloses, mostly mannose and xylose. Great quantities of different degradation compounds and extractives were also found from the condensed water as well as from the modified wood sample. Based on the chemical analyses, modified samples should be extracted before performing any tests since those compounds may vary the results.

Even though this experiment showed that the presumed hornification had no significant impact on the properties of thermally modified Scots pine under saturated steam, hornification is a phenomenon that should be understood better in the field of solid wood. There was at least indication that hornification might influence the EMC in thermally modified wood, which is essential also for some other properties that were not measured in this thesis, such as biological resistance. Therefore, additional tests should be performed concerning the effect of hornification.

Keywords DVS, Hornification, Saturated steam, Scots pine, Thermal modification

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Tiivistelmä
Tämän työn tarkoituksena oli tutkia sarveistumisen vaikutusta kylläisessä höyryssä lämpökäsitellyn männyn ominaisuuksiin. Tutkimus toteutettiin männyn tuorepuunäytteille, joita lämpökäsiteltiin 160 °C ja 170 °C kylläisessä höyryssä kolmen tunnin ajan. Lämpökäsittelyn jälkeen näytteet kuivattiin 75 °C viidessä eri ilmankosteudessa: 0 %, 25 %, 50 %, 75 % and 95 %. Näytteistä testattiin tasapainokosteus 20°C ja 65 % ilmankosteudessa, iskunkesto, taivutuslujuus ja turpoama, ja arvoja verrattiin kirjallisuuteen. Sarveistumista mitattiin puolestaan deuterointi-menetelmällä DVS-laitteessa. Kyseistä menetelmää myös kehitettiin tässä työssä, ja kehityksen tuloksena mittaukseen lisättiin kostutusvaihe sekä deuterointi-ajaksi 12 tuntia. Myös HPAEC ja GC-MS –analyysit tehtiin reaktoriin kondensoituneelle vedelle ja asetoniin liukeneville aineille lämpökäsitellystä puusta sekä käsittelemättömästä puusta.

Tuloksien perusteella tasapainokosteus muuttui kuivauksesta riippuen 160 °C lämpökäsittelyssä, mutta samaa ei ollut nähtävissä 170 °C lämpökäsittelyssä. Hydroksyyliryhmien saavutettavuutta mitattiin DVS-laitteella 160 °C näytteistä, jotka kuivattiin ilmankosteudessa 50 % ja 95 %. Näiden välillä havaittiin merkittäviä eroja. Tästä pääteltiin, että sarveistuminen saattaisi riippua ensimmäisen kuivausvaiheen kosteudesta. Tilastollisesti merkittäviä eroja ei kuitenkaan havaittu mekaanisissa testeissä tai turpoamatestissä. Kemialliset analyysit antoivat viitettä siitä, että kondensoitunut vesi sisälsi paljon hemiselluloosia, kuten mannoosia ja ksyloosia. Myös paljon erilaisia hajoamistuotteita ja uuteaineita löytyi vedestä sekä lämpökäsitellystä näytteestä. Löydösten perusteella lämpökäsitellyt kappaleet pitäisi uuttaa ennen mitään testejä, sillä hajoamistuotteet ja uuteaineet saattavat vaikuttaa tuloksiin.

Huolimatta siitä, että tässä työssä oletettu sarveistuminen ei vaikuttanut merkittävästi lämpökäsitellyn männyn ominaisuuksiin, sarveistuminen ja sen mekanismit tulisi ymmärtää paremmin puumateriaalissa. Työssä löydettiin viitteitä siitä, että sarveistuminen voisi vaikuttaa ainakin lämpökäsitellyn puun tasapainokosteuteen. Tasapainokosteus vaikuttaa moniin puun ominaisuuksiin, myös esimerkiksi biologiseen kestävyyteen, jota ei tutkittu tässä työssä. Lisää tutkimuksia tarvitaan, jotta sarveistuminen ja sen vaikutukset pystytään ymmärtämään puussa.

Avainsanat DVS, Kylläinen höyry, Lämpökäsittely, Mänty, Sarveistuminen

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First, I would like to express my sincerest thanks to the supervisor of my thesis, Professor Lauri Rautkari, for his guidance and invaluable help during this process. He has encouraged me, trusted me and guided me to the fascinating path of wood research. I will continue in this path after this thesis and therefore he deserves my deepest gratitude. I would also like to thank the instructor of my thesis and a good colleague of mine, Maija Kymäläinen, for the endless support and good comments that she gave me. She is my role model and the best teacher one can have when entering to the academic world.

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Tuuli Uimonen

Espoo 13.2.2017

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APPENDIX 1-4

LIST OF NOMENCLATURE

ANOVA	One-way variance analysis
ASE	Anti-shrink efficiency
CI	Confidence interval
DSC	Differential scanning calorimetry
DVS	Dynamic vapour sorption apparatus
EMC	Equilibrium moisture content
FSP	Fibre saturation point
FT-IR	Fourier transform infra-red
GC-MS	Gas chromatography-mass spectrometry
HPAEC	High performance anion exchange chromatography
ISEC	Inverse size-exclusion chromatography
MC	Moisture content
ML	Mass loss
MOE	Modulus of elasticity
MOR	Modulus of rupture
NMR	Nuclear magnetic resonance
OH	Hydroxyl
RH	Relative humidity
SA	Saturated pressure
TGA	Thermogravimetric analysis
WRV	Water retention value
WTT	Wood Treatment Technology

1 INTRODUCTION

Wood has many excellent material properties, such as good strength-weight relation and renewability, and therefore it is used for wide range of applications. However, it also has some disadvantages, such as tendency to dimensional changes and susceptibility to microbiological attacks. Thermal modification is a wood modification method where wood properties are permanently changed by applying heat. After the treatment, for example dimensional stability and resistance against microbiological attacks are improved in the wood material. This widens the applications for wood since thermally modified wood can be used for decking, cladding and in other moist environments where untreated wood fails. Still, thermal modification has an undesirable side effects since in most of the commercialized methods the mechanical properties of wood are decreased significantly during the process. Especially, impact strength and modulus of rupture (MOR) are decreased compared to unmodified wood. Therefore, thermally modified wood cannot be used in load-bearing applications.

There are many thermal modification methods commercially available and they are reviewed for example by Hill (2006). One way to sort these methods is to divide them by pressure regime, which consists of three categories: atmospheric, sub-atmospheric and elevated pressure regimes. Thermowood® is perhaps the most common example of atmospheric modification process, and Vacu and SmartHeat are examples of sub-atmospheric methods. (Altgen *et al.* 2016) In this thesis, atmospheric and sub-atmospheric methods are referred as traditional thermal modification methods. In them, the relative humidity is not controlled and the wood material dries during the treatment. On the contrary, the relative humidity can be controlled in elevated pressure methods and therefore drying of the wood material can be avoided (Altgen *et al.* 2016). There are two commercial methods using elevated pressure, Firmolin and WTT. There are also several peer-reviewed articles about thermal modification under elevated pressure. These articles use different names for the modification, such as thermal modification with pressurized steam, high-pressure steam, saturated steam or modification in highly moist conditions (Bhuiyan *et al.* 2000, Rowell *et al.* 2009, Ding *et al.* 2011a, Torniainen *et al.* 2013). However, all of them refer to the same kind of thermal modification where pressure is clearly over atmospheric pressure. In this thesis, names “thermal modification in high-pressure reactor” or “thermal modification with saturated steam” is used.

When wood is exposed to high temperatures, it degrades thermally and chemical changes take place. Chemical changes in the traditional thermal modification methods are widely researched (Tjeerdsma *et al.* 1998, Sivonen *et al.* 2002, Nuopponen *et al.* 2004). The degradation of cell wall polymers starts with cleavage of acetyl groups from hemicellulose. Those will form carboxyl acids, mainly acetic and formic acid, which will further catalyse the depolymerisation. (Tjeerdsma *et al.* 1998, Wikberg and Maunu 2004) Hydrolysis and dehydration take place in elevated temperatures, and aldehydes are formed again from hemicelluloses. Also, carbon dioxide is released during the degradation since there are decarboxylation reactions. (Hill 2006) Cellulose is hardly effected in the temperature range of thermal modification, but there is evidence that some of the amorphous cellulose is degraded which leads to increase of cellulose crystallinity, and therefore hydroxyl group accessibility is decreased (Sivonen *et al.* 2002, Wikberg and Maunu 2004). Lignin is resistant to thermal degradation in the modification temperatures, but it undergoes some important chemical changes, such as cross-linking, cleavage of ether linkages and demethoxylation (Tjeerdsma *et al.* 1998, Sivonen *et al.* 2002, Nuopponen *et al.* 2004).

Thermal modification in saturated steam causes some chemical differences to the wood material compared to traditional modification methods. One important difference is, that thermal degradation is proven to be faster in a closed high-pressure reactor (Seborg *et al.* 1953, Stamm 1956, Sundqvist *et al.* 2006, Torniainen *et al.* 2011). Therefore, same benefits of the end products are achieved with lower temperature and less time. Commonly, it is thought that degradation of hemicelluloses is behind the major changes in thermal modification. Recently, two other reactions are suggested to also affect to the changes in material properties: formation of inner tensions and irreversible hydrogen bonds referred as hornification (Borrega 2011). Hornification is a common term in pulp and paper industry but only recently brought to mechanical wood engineering (Suchy et al. 2010b, Rautkari *et al.* 2013a). There are few results indicating that hornification might have altered the mechanical properties of wood material, such as increased the toughness, but decreased for example the impact strength (Thuvander *et al.* 2001, Borrega and Kärenlampi 2010). However, the effect of hornification to the properties of solid wood, let alone to the properties of thermally modified wood, is far from been understood.

1.1 Research objective

The aim of this thesis is to investigate the effects of possible hornification in thermally modified wood in high-pressure reactor under saturated steam. Thermal modification in these conditions enables to control the possible hornification since the wood is not drying during the treatment unlike in traditional modification methods. Therefore, no hornification should occur during the modification. Hornification could in theory be favoured or un-favoured during the drying step after the modification. The assumption in this thesis is that hornification is increased with fierce drying and decreased with mild drying. This theory of hornification is tested and its effect on the thermally modified wood material investigated. However, there are no standardized testing methods to investigate hornification and its effects on solid wood. Therefore, developing a suitable measuring method for hornification in solid wood is an important part of this thesis. Also, a custom-built prototype of a high-pressure reactor was used for the modification, and the parameters for the modification needed to be found prior to the experiment.

1.2 Structure of the study

This work is divided in to two main parts: literature review and the experimental part. The aim of the literature part is to find information about thermal modification in high-pressure reactor under saturated steam (Chapter 2), and hornification in pulp, paper and wood (Chapter 3). In Chapter 4, the methods to measure hornification in cellulose and wood are reviewed and evaluated with the purpose of finding the best methods to be used for this thesis. The literature part should give a comprehensive, objective review and basic understanding on the topics of this thesis. This is achieved by using peer-reviewed articles and scientific books with critical consideration. The experimental part consists of a methodology part (Chapter 5) followed by results and discussion (Chapter 6). First in Chapter 5, the prototype of a high-pressure reactor is introduced and tested, followed by the development of the methods to measure hornification in solid wood. After that, the extent of hornification and its effects on the material thermally modified in high-pressure reactor are tested. Finally, some chemical analyses are performed. The results from all the experiments are reviewed and discussed in Chapter 6 in the same order as in Chapter 5. Experiments are then concluded and further research topics proposed in Chapter 7.

LITERATURE REVIEW

2 THERMAL MODIFICATION IN HIGH-PRESSURE REACTOR

One certain benefit of modification under saturated steam (SA) in a high-pressure reactor is that there is more water present during the modification than in traditional modification. It has long been known that degradation of wood polymers is faster in moist conditions than in dry conditions (Stamm 1956, Mitchell 1988). Also, closed system is noted to increase the thermal degradation (Stamm 1956). This Chapter aims to give a short but comprehensive review on the state of thermal modification in high-pressure reactor under saturated steam. First two commercial processes are introduced, within the limits of available information. Then the effects of saturated steam and high-pressure reactor to the wood material are discussed based on the literature.

2.1 Commercial processes

There are two commercial processes available for thermal modification in a high-pressure reactor. Firmolin is first reviewed in section 2.1.1 and shortly evaluated. Wood Treatment Technology (WTT) is then introduced in section 2.1.2. The material properties for both the methods are reviewed in the section 2.2.

2.1.1 Firmolin

Firmolin is a thermal modification method developed and patented by Willems (2013). There is a production plant in the Netherlands using this method, at FirmoLin Technologies BV (Willems 2009). The apparatus used in the Firmolin process is in Figure 1. The modification place in the reactor is first vacuumed and then filled with steam from the steam generator. The temperature of the walls and the wood material is controlled with a thermostat and a heating device to keep it higher than the vapour dew point temperature to avoid condensation. Temperature rise is limited to 20–69 °C per hour and the pressure saturation maximum is 95%. (Willems 2013)

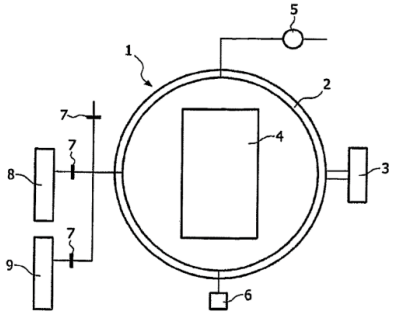


Figure 1: *Firmolin apparatus. Numbers stand for: 1) modification place, 2) thermally conducting oil, 4) wood material, 5) vacuum pump, 6) measuring and control equipment, 7) control valve, 8) and 9) steam generators. (Willems 2013)*

After the treatment, wood is dried with the same equipment to MC of 3–5 % and then cooled to EMC of 7–8 %. According to the patent, ideal material for this modification method is spruce wood (*Picea Abies*) in 25 mm thick planks. However, also pine wood is mentioned as a potential material. Material with larger dimensions can also be treated but the treatment time increases with increased dimensions. The modification time in steam is 4 hours for the ideal material, and during that time the temperature is increased from 20 °C to 180 °C (40 °C per hour). Therefore, the reaction time is only around 15 minutes at high temperature and 9 bar pressure. The whole process takes 10 hours including heating and cooling, which can be seen from Figure 2a. (Willems 2013) The working conditions for the process are in Figure 2b.

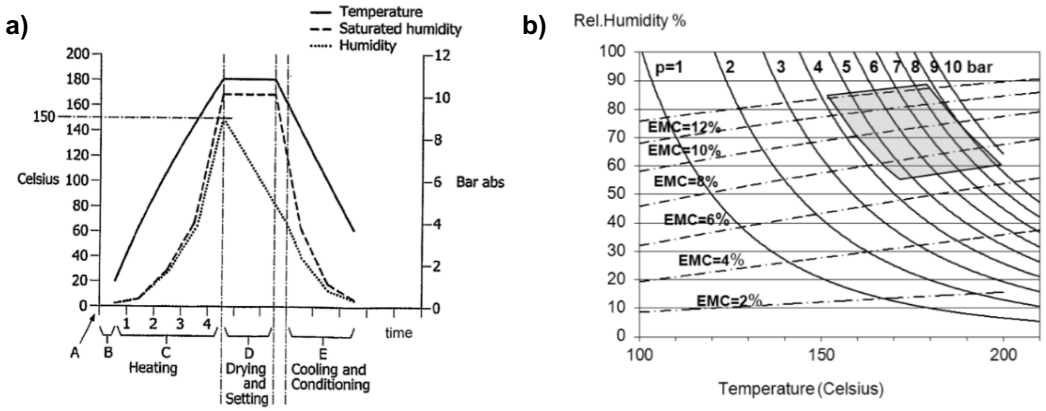


Figure 2: a) *Firmolin process steps. Letters stand for A) wood is placed in the reactor, B) vacuum is created and boiler pre-heated to 70 °C, C) steam is supplied, D) pressure is reduced, E) cooling state. (Willems 2009)* ***b)*** *Working conditions for Firmolin process. (Willems 2013)*

The pressure equipment used in the Firmolin process is expensive compared to the kilns used in traditional thermal modification methods. Also, additional costs are caused by the disposal of water and polluting organic substances that are released from wood during the Firmolin process. However, there are also several factors reducing the costs of the Firmolin modification compared to traditional methods, such as decreased modification time, moderate temperature and lower quality requirements concerning the raw material. (Willems 2009) Based on the references, the Firmolin process is an appealing wood modification method and it has potential over the traditional methods. However, the only available information about the method is from articles written by the inventor, Willems. It would be essential to have also other information sources to form an objective opinion about the process.

2.1.2 WTT

WTT stands for Wood Treatment Technology, the name of the Danish company producing high-pressure autoclaves for thermal modification of wood. There is limited information about the process and most of the information is from Dagbro *et al.* (2010) who used WTT apparatus in their studies. Therefore, an objective review is not achieved as was the case with the Firmolin prosess. The apparatus made from stainless steel (Figure 3a) is heated by a radiator inside the cylinder. Water feed generates steam into the tube and some of the evaporated water is removed in the middle of the process. The process parameters are in Figure 3b. The pressure can reach up to 10 bars in the peak of the process where temperature is kept 160 °C–180 °C. The wood material stays wet during the process and has 10–15% of residual moisture after the process. (Dagbro *et al.* 2010)

a) **b)**

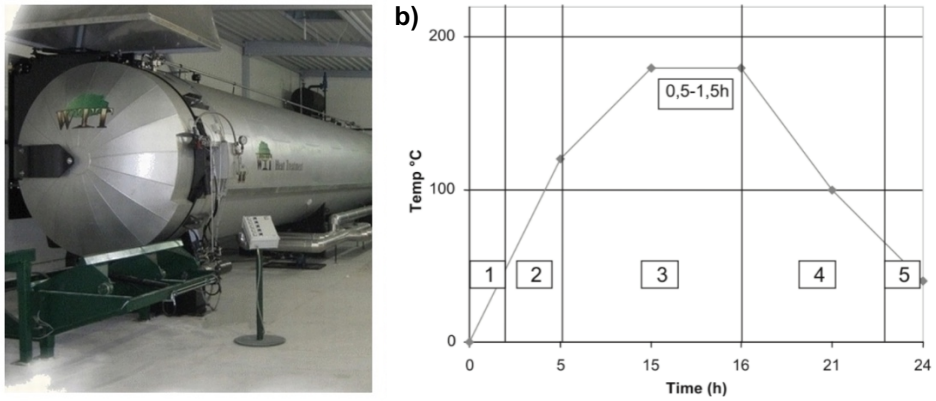


Figure 3: a) *WTT apparatus. (WTT 2010)* ***b)*** *WTT process at 180 °C. Numbers stands for: 1) prevacuum, 2) heating, 3) thermal modification under pressurized conditions 4) cooling 5) pressure normalization. (Dagbro et al. 2010)*

Dagbro *et al.* (2010) thought the pressurized steam process needs to be improved regarding the repeatability of the process and to improve the material quality. Problem seemed to be that residual moisture content was substantially high in the material and therefore it needed to be dried before end use. They suggested that the material could also be dried before the modification since the moisture content after WTT modification was related to the initial moisture content of the material. Moisture content of the wood correlates with the properties of the material and therefore it has a great effect on which temperature the sample is dried at after modification. Moisture content of wood strongly correlates with the mechanical properties of wood. (Gerhards 1982)

2.2 Effect of the high-pressure steam

Degradation and chemical changes due to thermal modification affect the physical, biological and mechanical properties of wood. The extent of the changes is tied to many parameters in the modification process such as the process temperature, time and atmosphere (Hill 2006 s. 100, Ding *et al.* 2011a, Navi and Sandberg 2012 s. 250). Also, the material properties such as moisture content, species, sapwood versus heartwood, have a great impact on the end products (Hill 2006, s. 100). In this Chapter, the focus is on the modification under pressure that is over the atmospheric pressure. Therefore, the impact of closed system, pressure and moisture are reviewed and the effect of other factors in the process, such as material properties, are ruled out.

2.2.1 Chemical and physical changes

Thermal modification in high-pressure reactor leads to different physical properties of the material when compared to the traditional modification processes. Differences can be seen in properties such as colour, mass loss and the crystallinity degree of the cellulose. The reasons behind this changes are in chemical changes of the wood material and therefore it is essential to understand what happens during the modification under high-pressure steam.

Decreased holocellulose content and loss of free hydroxyl groups are achieved to a greater extent with pressurized steam than with atmospheric steam (Ding *et al.* 2011b). Main reasons for these differences is the presence of water, and the closed system which accelerates the degradation as mentioned earlier. The effect is due to the acids, mainly acetic acid, formed from the O-acetyl groups of hemicellulose which cleave when exposed to high temperatures (Fengel and Kollmann 1965, Garrote *et al.* 1999). Water molecules in the process are believed to accelerate forming of organic acids, such as acetic acid, by autoionization (Garrote *et al.* 1999). Acetic acid acts as a catalyst for hydrolysis of the hemicellulose to soluble sugars (Hillis 1984, Schultz *et al.* 1984). In a closed system, the formed acetic acids also stay in the reactor and further accelerates the hydrolysis (Stamm 1956, Sundqvist *et al.* 2006). This is supported by the fact that higher acid content was found in modification under saturated condition than in the traditional method (Torniainen *et al.* 2011).

Naturally, the mass loss is greater in SA modification than in traditional modification since mass loss is mostly due to the degradation of hemicelluloses which is accelerated in SA modification (Hill 2006, s.111, Rautkari *et al.* 2014). Mass loss is also increased by the

effect of closed system (Mitchell 1988). Anti-shrink efficiency (ASE) values for saturated pressure treatment have also been found quite high, relatively higher than in atmospheric treatment (Seborg *et al.* 1953, Rautkari *et al.* 2014). Results are logical since the water uptake has a close relationship with free hydroxyl groups in amorphous polysaccharides. Therefore, with increased degradation of hemicellulose, the hydrophilic parts in wood are decreased. (Rowell *et al.* 2009, Ding *et al.* 2011b) Also, lignin is suggested to undergo some chemical changes in combination of water and elevated temperatures. Increased dimensional stability could be also partially from increased cross-linking in lignin. (Ding *et al*. 2011b)

Cellulose is more thermally stable than hemicelluloses but the presence of water in elevated temperatures increases the probability of chemical changes and degradation also in cellulose (Möller and Otranen 1999, Hill 2006 s. 107) Increase in the crystallinity of the cellulose has been noticed when treated in moist rather than dry conditions (Dwianto *et al.* 1996, Bhuiyan *et al.* 2000). Molecular mobility increases in the presence of water, and additional release of stresses due to partial degradation of wood components would favour the rearrangement of cellulose molecules in the amorphous regions. Both occur since there are less stresses in wood components under moist conditions than under oven-dry conditions. Also, it has been calculated that activation energy for crystallization is lower in moist conditions and therefore is more likely to occur. (Bhuiyan *et al.* 2000). Ding *et al.* (2011b) noticed the same with FTIR spectrometer.

The colour of the wood material has been noticed to be darker after SA modification than after traditional modification (Dagbro *et al.* 2010, Torniainen *et al.* 2011, Ding *et al.* 2011a). Redness was also more dominant after high-pressure modification than after traditional process, whereas yellowness was the other way (Dagbro *et al.* 2010). Colour of thermally modified wood have been found to correlate with degradation of hemicellulose and lignin (Esteves *et al.* 2008).

2.2.2 Mechanical changes

Wood thermally modified with the traditional method suffers from the loss of mechanical properties, especially impact strength and MOR, as mentioned earlier. Since thermal modification in high-pressure steam results to different chemical and physical properties of the material compared to traditional modification, it can be expected to differ also in mechanical properties. Mitchell (1988) stated that the mechanical property loss in wood was greater in the presence of water, except with residual hygroscopicity. He found that

MOR and modulus of elasticity (MOE) values both decreased with increased water in the process. Similarly, Torniainen *et al.* (2011) noticed that bending strength decreased greatly in SA treatment. Rautkari *et al.* (2014) also found a 30% decrease in MOR when SA modified at 180 °C. However, they also found that when modified at 150 °C with SA, MOR increased 15%. MOE, on the other hand, neither decreased nor increased significantly in their studies. Also, Brinell hardness stayed on the same level with untreated samples. (Rautkari *et al.* 2014)

Ding *et al.* (2011a) found that mechanical properties after SA modification where rather similar with the properties produced by the traditional modification. This is again in a disagreement with other results where toughness improved compared to traditional treatment. SA modified samples had up to 31% decrease in toughness whereas traditionally modified samples suffered from s decrease up to 80%. (Boonstra *et al.* 2007, Rautkari *et al.* 2014) The Firmolin patent claims that after the modification, mechanical strength is decreased by 10% to 15% (Willems 2013). Using the same method Willems (2014) proved that there are no internal of external cracks formed during the process since the material is not drying. He also claimed that defects already present in the wood material stay unchanged during the process, and therefore mechanical properties are indirectly increased. (Willems 2014)

Borrega and Kärenlampi (2008) had an interesting suggestion that since thermally modified wood has lower hygroscopicity, it may have some better mechanical properties than untreated wood has. He found that samples that were modified at an intermediate RH, around 50%, were strongest and stiffest. They also had greatest inelastic ductility and inelastic toughness. (Borrega and Kärenlampi 2008) All in all, there is no agreement in the literature what happens to the mechanical properties of wood when thermally modified with high-pressure steam. Therefore, more research is needed regarding this topic.

3 HORNIFICATION

Hornification is widely used term in pulp and paper industry where it has been concluded to have a high impact on the pulp and paper properties (Kato and Cameron 1999, Šutý *et al.* 2012, Heijnesson-Hulten *et al*. 2013). Recently, the phenomenon has been suggested also for solid wood (Suchy et al. 2010b, Rautkari *et al.* 2013). This Chapter aims to explain the phenomena behind hornification first from the cellulose fibre aspect and then from the aspect of solid wood.

3.1 Hornification in pulp and paper research

Hornification is explained in few different ways in the literature of pulp and paper. Most commonly, it is said to refer to the stiffening of the material during water removal from the fibre cell walls (Diniz *et al.* 2004, Hubbe *et al.* 2007) However, some might use the name “hornification” for any occasion where any stresses are applied to fibres (Hubbe *et al.* 2007). Hornification is also referred to as irreversible cellulose microfibril aggregation (Pönni *et al.* 2014).

The mechanism behind hornification is not agreed in literature. It has been more and more accepted that it is due to the formation of irreversible hydrogen bonds when water is removed from wood pulp or paper (Smook 1990). Increasing hydrogen bonding is proposed to be possible due to the collapse of pores that are between cellulose microfibrils, or tighter packing of cellulose chains during the water removal. (Suchy 2011) Suggested hydrogen bonding in cellulose is demonstrated in Figure 4. Hydroxyl groups in cellulose enable the formation of inter- and intramolecular hydrogen bonds. In Figure 4, there are two kinds of intramolecular hydrogen bonds, the other between oxygen and hydroxyl group of carbon 4 (C4) and the other between hydroxyl groups of C6 and C2. The existence of the latter one is disagreed in literature (Krässig 1993). The degree of hornification is therefore greatly related to the accessibility of the hydroxyl groups in cellulose. Decrease in hydroxyl groups accessibility indicates increased hornification.

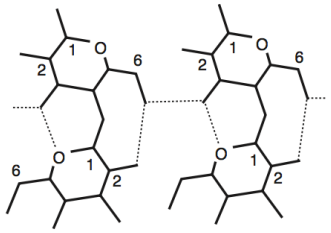


Figure 4: *Inter- and intramolecular hydrogen bonding in cellulose. Proposed hydrogen bonds are marked with dashed lines. (Cato and Cameron 1999).*

Also, other mechanisms of hornification are suggested such as closure of capillaries (Suchy 2011). For example, Diniz *et al.* (2004) strongly believed that hornification cannot be explained by hydrogen bonding since the bonds are broken by water. In the paper, they suggest a theory that covalent lactone bridges are responsible for hornification. It was explained that when water is removed, carboxylic acid groups (from lignocellulose) are interacting with hydroxyl groups and form covalent lactone bridges. The conclusion was based on the result that alkaline solutions and sodium borohydride reduce hornification. Alkaline solutions and sodium borohydride are said to cleave hemiacetal bonds, known as lactone bridges. (Diniz *et al.* 2004) The theory did not receive support since there are many questions which it cannot answer such as why hornification is favoured in chemical pulps with very low yield (Hubbe *et al.* 2007).

Evidently, hornification is not fully understood and agreed in the literature. Despite that, Figure 5 demonstrates one widely accepted model of fibre drying introduced first by Scallan (1977) and reviewed by Cato and Cameron (1999). When a virgin fibre is dried for the first time, the re-wetting does not result to the same morphology of the fibre. Because of hornification, the fibre swelling is limited after the first drying and that effects on the other properties of the paper. The outcome is stiffer fibres and therefore stiffer paper. This results to lowered bonding potential and decreased strength properties in paper. (Heijnesson-Hulten *et al*. 2013) Especially, brittleness of paper is increased (Šutý *et al.* 2012).

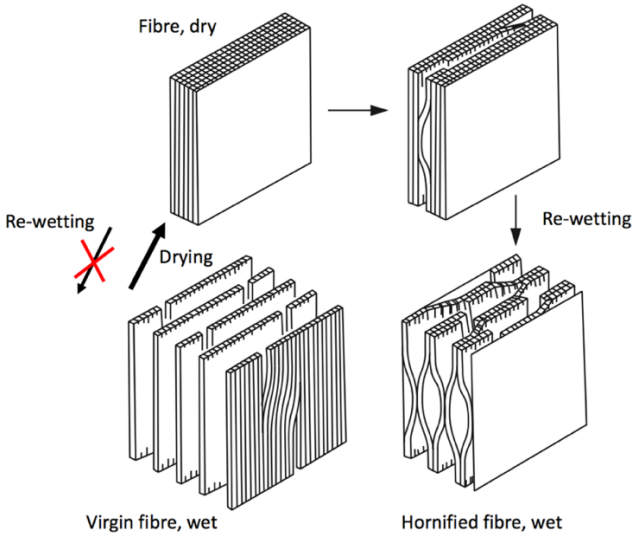


Figure 5: *Model of the fibre re-wetting modified from Cato and Cameron (1999).*

Despite the disagreement with the mechanism, hornification is demonstrated to occur below fibre saturation point (FSP) (Laivins and Scallan 1993). FSP is a state where fibre has water only in the cell wall, and there is no free water in the lumen (Hill 2006). Hornification is found to be determined mainly by the water removal and the temperature has only a minor effect to it (Cato and Cameron 1999). Based on several works, the rate of hornification also depends on the hemicellulose content of pulp, and with increasing content the hornification is decreased because of spatial intervention (Oksanen *et al.* 1997, Östlund *et al.* 2010).

3.2 Hornification in wood research

There is limited research about hornification in solid wood and it has not been confirmed whether hornification occurs in solid wood or not. However, there are few studies indicating that similar reaction takes place. Suchy *et al.* (2010a) noticed that water accessibility changes during the drying of green wood and they thought it had to be due to the rearrangements of the wood polymers. They had two hypotheses: “irreversible aggregation of cellulose microfibrils in a similar manner (but to a smaller extent) that occurs during hornification of pulp fibers” and “irreversible stiffening of the hemicellulose/lignin matrix that extensively swells when exposed to water”. (Suchy *et al.* 2010a) In addition, Borrega and Kärenlampi (2010) were convinced that hornification occurs in solid wood but they did not take a stand on to what extent.

It can be assumed that the hornification in solid wood is rather similar than in paper and pulp. However, the greatest difference is that there are more compounds besides cellulose, such as hemicelluloses and lignin, in wood than in pulp. As reviewed in the previous section, hemicelluloses are believed to decrease hornification since they are located between the cellulose microfibrils and aggregating is therefore decreased (Oksanen *et al.* 1997). Also, it has been noticed that removing lignin increases the hornification due to the greater percentage of cellulose (Suchy *et al.* 2010b). Therefore, hornification can be expect to have less impact in solid wood than in pulp or paper.

However, hornification in thermally modified wood is different from unmodified wood. The greatest distinction is that hemicellulose content is decreased compared to solid wood. Hypothetically, this could increase hornification if such a phenomenon is to occur in thermally modified wood. Traditional thermal modification will supposedly increase hornification due to the total dryness and high temperature. However, thermal

modification in saturated conditions would prevent hornification and the degree of hornification could therefore be controlled up to some extent with drying after the modification. This is a hypothesis that has not been investigated yet in the literature. Nevertheless, Cato and Cameron (1999) suggested hornification to take place during thermal modification of pulp. However, they suggested the reaction happens in the amorphous regions of cellulose and hemicelluloses, which are decreased in the thermally modified wood as reviewed in section 2.2.1.

4 MEASURING HORNIFICATION

In this Chapter, the most common methods to measure hornification are reviewed. However, the methods do not give an unambiguous number for hornification but it can be indicated by the accessibility of the hydroxyl groups in cellulose or in wood material, as reviewed in section 3.1. The less there are accessible hydroxyl groups, the greater is the degree of hornification. The methods reviewed here are divided to two categories: 1) “indirect methods”, which are shortly discussed in section 4.1, and 2) so called “direct methods”, described in section 4.2. Indirect methods are based on the measurements that only give a guess about the number of accessible hydroxyl groups based on some other property such as pore size and shape. Direct methods on the other hand measure directly the accessibility of the hydroxyl groups.

4.1 Indirect methods

There are many indirect methods to measure hornification and most of them are related to the accessibility of cellulose. This means that some other property is measured and accessibility is more or less related to that property and through that, hornification can be estimated. In Table 1, the indirect methods that can be used for estimating hornification are qualitatively analysed. These methods are applied to measure hornification in pulp.

Table 1: *Advantages and disadvantages of indirect methods to measure hornification.*

Method	Source(s)	Advantages	Disadvantages
WRV	Jayme 1944, Weise 1998	Simple, standardized	Not suitable for solid material
Solute exclusion (FSP)	Stone and Scallan 1968	Good for FSP estimation	Time consuming, unreliable results
ISEC	Berthold and Salmén 1997	Faster than solute exclusion	Unreliable results
NMR relaxometry	Häggkvist et al. 1998	Accurate	Data is hard to interpret
NMR cryoporometry	Östlund et al. 2010	Accurate	Expensive equipment
Thermoporosimetry	Maloney et al. 1998, Park et al. 2006	Simple and ready technique	Unreliable results

Water retention value (WRV) is widely used method in pulp and paper industry and it was first introduced by Jayme (1944). WRV is strongly connected to the hornification of pulp, and hornification has been even described as a decrease in WRV (Laivins and Scallan 1993). The method has been standardized to ISO 23714 (2007). WRV describes the amount of water that stays in the pulp after centrifugal forces have been applied (Pönni *et al.* 2014). The greater the amount of retained water, the more there are accessible hydroxyl groups in the cellulose and the less the pulp is hornified. However, WRV cannot be adjusted to solid wood since centrifugal forces are not removing the water from solid wood samples the same way as from wet pulp.

One way to estimate hornification is to analyse the pore size of the sample. Pore size is related to hornification up to some extent. The smaller and more collapsed the pores are the greater is the probability of hornification. Basic pore measurement methods analyse the average pore size and its distribution. However, the results are not truly reliable since the pores are mostly irregularly shaped and poor approximations are used in the calculation. (Maloney and Paulapuro 1999, Park *et al.* 2006) There are many methods based on the pore size measuring and the most common ones are in Table 1: Solute exclusion, Inverse size-exclusion chromatography (ISEC), nuclear resonance spectroscopy (NMR) and thermoporosimetry.

Solute exclusion has been used for long time to investigate the structure of fibre pores (Stone and Scallan 1968). It is a good method to evaluate the amount of water in the cell wall and it is sometimes referred as a fibre saturation point (FSP) measurement since the measurement is done under fully swollen state of the fibre (Park *et al.* 2006). The measurement is based on the assumption that probe molecules (soluble mono- and

polysaccharides) can access all the pores that are larger than the diameters of the probes and therefore, accessibility of noninteracting pores can be measured. (Maloney and Paulapuro 1999) The method has some disadvantages such as ignoring the small and isolated pores and the fact that it requires several experiments and is therefore time consuming (Berthold and Salmen 1997, Park *et al.* 2006). ISEC is using the same principle as solute exclusion and is also done in the swollen state of the fibre. The difference is that ISEC provides more data with just one experiment the solute exclusion method. (Berthold and Salmen 1997)

Thermoporosimetry is a technique where differential scanning calorimetry (DSC) is used for pore size distribution measurement. The method is applied for pulp fibers by Maloney *et al.* (1998). It is based on the phenomenon that water that is inside the pores has depressed melting temperature compared to free water molecules. However, also osmotic pressure results to depression in water melting temperature and therefore the results are not unambiguous. (Maloney 1998, Maloyne and Paulapuro 1999) DSC can be combined with TGA to get more accurate results (Park et al. 2006).

NMR is also used to analyse the pore structure in cell walls, and one type is NMR relaxation method. The relaxation time in NMR is shorter for liquid molecules close to solid base than for separate liquid molecules. Therefore, NMR signal is dependent on the pore volume and the pore surface area ratio can be estimated. (Häggkvist *et al*. 1998) The greatest disadvantage is that the data is difficult to interpret. (Maloney and Paulapuro 1999) A more recent method is NMR cryoporometry which is following the same principle as thermoporosimetry. NMR cryoporometry has successfully been used to study hornification in pulp. (Östlund *et al.* 2010).

As seen from Table 1, there are many limitations in the indirect methods when using them for estimating hornification. If measuring the hornification in pulp fibres, a good estimation might be reached with combining WRV to one of the pore size distribution methods. However, with these methods, no value or quantitative analysis can be given for hornification. Also, WRV cannot be applied to solid wood and therefore other methods are needed for estimating hornification in solid wood.

4.2 Direct methods

There are two methods that measure exclusively the accessibility of hydroxyl groups in the material: deuteration combined with Fourier transform infra-red (FT-IR) spectroscopy and dynamic vapour sorption (DVS) –method. The accessibility of hydroxyl groups in wood and pulp is inversely proportional to the hornification and therefore these two methods are referred as direct methods. With direct methods, hornification results are more reliable since no second-hand property is used for the estimation.

4.2.1 Deuteration combined with FT-IR spectroscopy

Deuteration combined with FT-IR has been used to study different properties of cellulose such as diffusion and effects of moisture uptake (Tsuchikawa and Siesler 2003, Hofstetter *et al.* 2006). Suchy *et al.* (2010a) implemented the method to measure accessibility of cellulose during different treatments. The method combines deuteration step with photoacoustic (PAS) FT-IR analyses. The concept is demonstrated in Figure 6. The first step is to exposure the sample to D_2O which cause the OH groups change to OD groups. Suchy *et al.* (2010a) dried the sample after that to get some of the OD groups inaccessible and those retained in the sample after washing the sample with water.

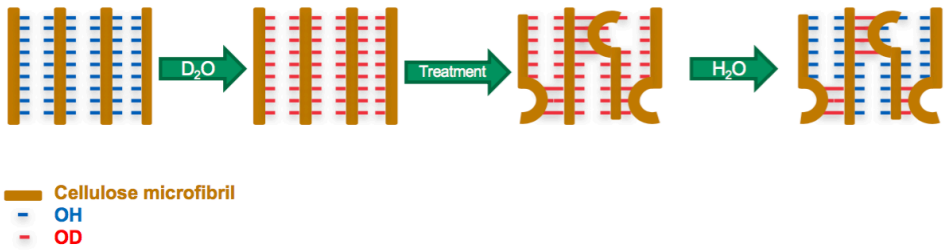


Figure 6: *Scheme of the deuteration method illustrated by Pönni et al. (2014).*

OD groups left in cellulose could after Figure 6 be appointed with IR spectroscopy. Deuterium stretch signal is located at 2500 cm^{-1} as can be seen from the FT-IR spectra in Figure 7. There are no other signals near this peak and interpreting the spectra is therefore rather easy. (Suchy *et al.* 2010a) The result got from the method is an estimation of the hydroxyl groups that are inaccessible in the material. Therefore, the results are directly proportional to the extent of hornification.

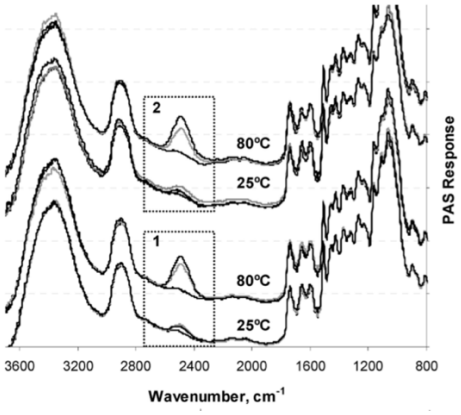


Figure 7: *FT-IR spectra of pine (upper) and spruce (lower) dried in to different temperatures. Squares indicate where deuterium peak is seen. (Suchy et al. 2010a)*

Even though the method bares information about the hornification, precise number of accessible hydroxyl groups is not achieved (Pönni *et al.* 2014). Therefore, the comparison of results from different experiments is not possible. Also, the method should be standardized since for example, if the deuteration time differs in the experiments, it has a great impact to the results (Suchy *et al.* 2010a).

4.2.2 DVS

Accessibility of hydroxyl groups in wood can be measured by deuterium exchange in dynamic vapour sorption apparatus (DVS) (Rautkari *et al.* 2013, Pönni *et al.* 2014, Popescu *et al.* 2014, 2015, Kymäläinen *et al.* 2015). The principle of the method has long been known for cellulose (Sepall and Mason 1961) but the apparatus was commonly used to investigate the water sorption behaviour of wood and fibres (Hill *et al.* 2010, 2012) rather than accessibility.

The DVS method is based on the exchange of protium (1H) from free hydroxyl groups to deuterium (2H). This will increase the mass of the sample since deuterium has 1 g/mol higher atomic mass than hydrogen due to the additional neutron (Pönni *et al.* 2014) as can be seen from Figure 8a. Figure 8b demonstrates how only the free hydroxyl groups will exchange their hydrogen and those who are not accessible will attain the normal hydroxyl groups.

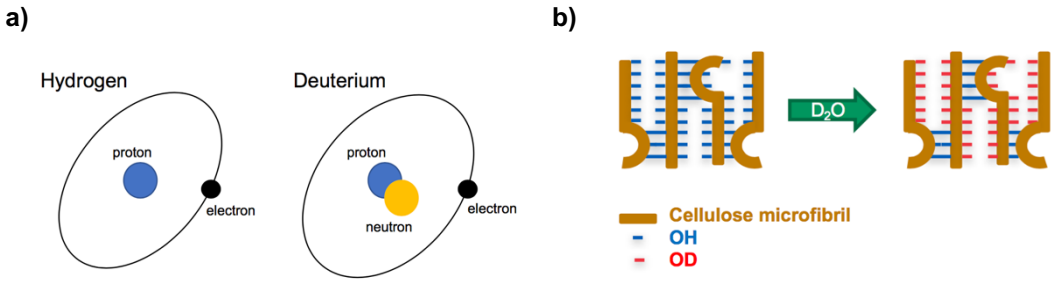


Figure 8: a) *Difference of hydrogen and deuterium atoms.* ***b)*** *Change of hydrogens from free hydroxyl groups to deuterium (Pönni et al. 2014).*

Pönni *et al.* (2014) concluded that DVS is a reliable method to measure cellulose accessibility. The greatest advantage of the method is that actual number for accessible hydroxyl groups is achieved. However, the long measurement time is a major weakness of the method (Pönni *et al.* 2014). There is too little information, for example, about the proper deuteration time of the sample, even though Pönni *et al.* (2014) noticed it to have great effect to the accessibility results. Also, the DVS method would need some standardization to get more comparable results. Compared to deuteration and FT-IR methods, standardizing the DVS method is rather simple since the steps are done in the programmed apparatus and not by hand.

EXPERIMENTAL PART

5 METHODOLOGY AND PRELIMINARY RESULTS

The aim of this thesis was to investigate possible hornification in wood that is thermally modified in high-pressure reactor. Therefore, Scots pine was eventually thermally modified under saturated steam and dried after the process, after which the equilibrium moisture content (EMC), mechanical and swelling properties were tested. Also, accessibility of hydroxyl groups was measured with DVS to get an indication of hornification. However, before starting the actual experiment, preliminary tests needed to be executed and a DVS method developed to fit the purposes of this thesis. The results from these preliminary tests are reviewed in this methodology part to keep the structure explicit. This Chapter is therefore divided into four parts. In the first section, a new high-pressure reactor is introduced. In the second part of this Chapter, the method for accessibility measurements with DVS apparatus is developed. Third section includes the actual testing on the effects of hornification. In the last part, chemical analyses are explained.

5.1 Introduction of high-pressure reactor

In this section, a new high-pressure reactor is introduced and pre-test for mass loss and relative humidity during the modification are explained. The aim of these experiments was to learn to use the reactor and find suitable parameters to use in the following experiments in this thesis. Results for mass loss test are discussed here since the results are essential for further experiments.

5.1.1 Reactor

A high-pressure reactor for thermal modification of wood was built in Aalto University School of Chemical Technology and is photographed in Figure 9a. The actual reactor is 20 litres but the apparatus consists a separate evaporator that holds 4 litres of water. Thermal modification is performed with water vapour controlled through that evaporator. Flowchart of the apparatus is in Figure 10. Temperature in the reactor is monitored with three thermometers, and the pressure with a pressure sensor. Automatic valve will open if the pressure is increased over the set point. The basket for the samples is seen in Figure 9b where it is loaded with test specimens.

a) b)

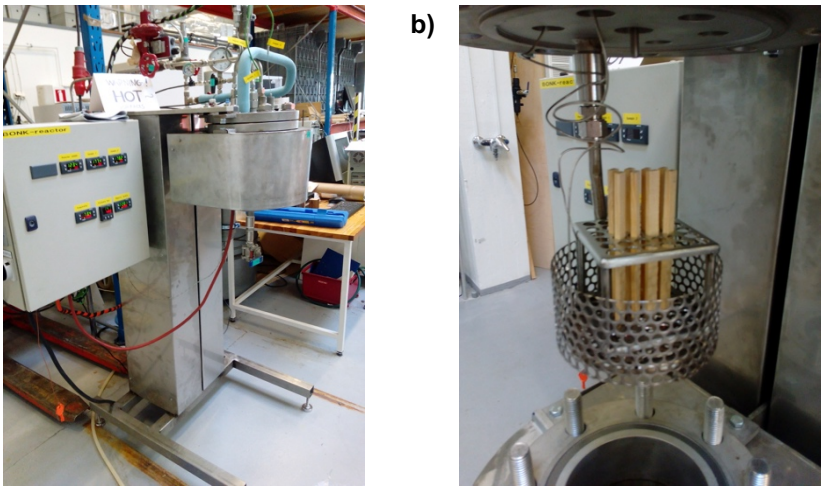


Figure 9: *Loaded high-pressure reactor* ***a)*** *closed* ***b)*** *open.*

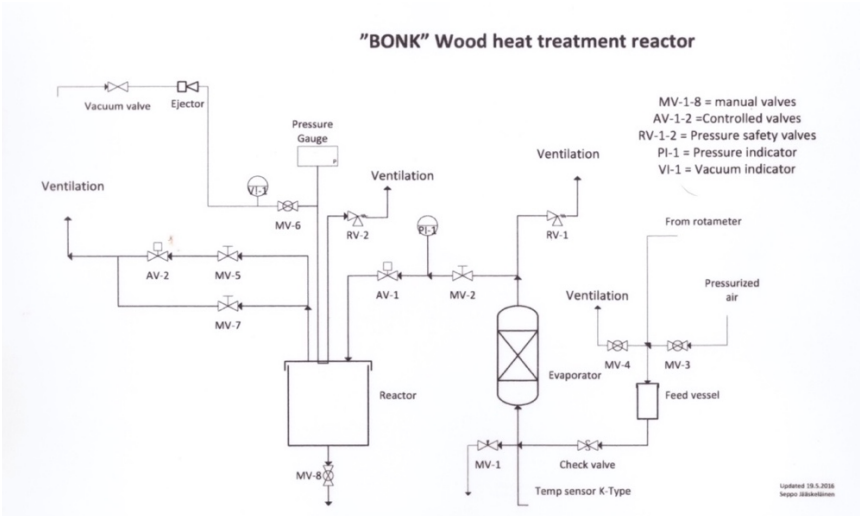


Figure 10: *Detailed flowchart of the high-pressure reactor.*

5.1.2 Material information

Material used in this pre-test section was Scots pine (*Pinus sylvestris L.*) grown in Finland. Only sapwood boards were chosen. Boards were conditioned several months at 20 °C and RH 65% and then cut and planed to specimens of 13 cm longitudinal, 1 cm radial and 0.5 cm tangential. Samples with knots and cracks were eliminated. The samples were first dried at 50 °C oven for 24 hours in order to avoid cracks and then at 103 °C oven for 24 hours. Oven-dried weight was measured and samples market carefully. Half of the samples were soaked in water for few days and half of them were kept in the oven. The soaked samples are referred as “wet samples” and oven-dried ones as “dry samples”. Wet samples were included to the experiments to indicate the possible changes in green wood that is tested later in this thesis.

5.1.3 Mass loss experiment

In order to start any actual testing, a proper temperature had to be found to obtain a desired mass loss. Mass loss was aimed was between 3 to 8% since according to the patent of Viitaniemi *et al.* (1997) that is the limit where the benefits of thermal modification are achieved. Based on the gained mass losses of Rautkari *et al.* (2014), five temperatures were tested (140, 150, 160, 170, 180 °C) at saturated vapour pressure. Samples were thermally modified in the high-pressure reactor introduced in section 5.1.1.

Th reactor and evaporator were pre-heated about 1 hour to reach the modification temperature. Then the lid was opened, loaded with samples and closed again within 5 minutes. Temperature was lowered to under 100 °C but target temperature was reached again rather quickly when the programme started. Six dry samples and six wet samples were tested in each temperature. Temperature and saturated vapour pressure were kept in the reactor for 3 hours. Water was removed from the process after 1 hour and after 2 hours. Reactor was manually stopped at the end of the process and samples taken away. Example of the treatment conditions can be seen from Figure 11. The pressure was stabilized within 15 minutes of beginning and stayed in the set value for the whole treatment. Temperature was adjusted within 30 minutes of starting but small variations were seen also after the start. Temperature was on average 2 °C higher than the set value which is not a remarkable difference.

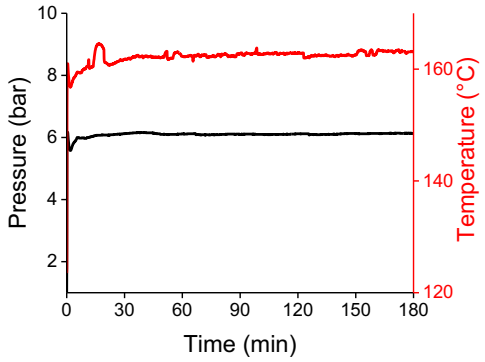


Figure 11: *Process conditions for set values of 160 °C and 6,18 bars.*

Samples were then dried again at 103 °C for 24 h and a new oven-dry weight was measured. The mass loss was calculated following the Equation 1 where m_{OD1} stands for the initial oven-dried weight and m_{OD2} for the oven-dried weight after the heat-treatment.

$$\text{Mass loss } (\%) = \frac{m_{OD1} - m_{OD2}}{m_{OD1}} \cdot 100\ \% \quad \textbf{(1)}$$

Results showed an expected increase in mass loss with increased temperature (Figure 12). Wet samples resulted in greater mass loss, also as expected. Based on this results, proper temperatures had to be found for further tests. With 140 °C the results were unreliable and there was a lot of variation, therefore it was not a proper temperature. With 150 °C the mass losses were quite small and decreasing the relative humidity would lead to no mass loss at all. However, 180 °C resulted to too great mass losses and the wood samples were extremely brittle after the modification. Eventually, 160°C and 170°C, with corresponding mass losses of around 6 and 12%, were chosen for further tests since 160 °C was the only temperature where aimed 3–8% mass loss was reached. 170 °C was also chosen as a comparable temperature because with decreasing RH the mass loss would approach the aimed values.

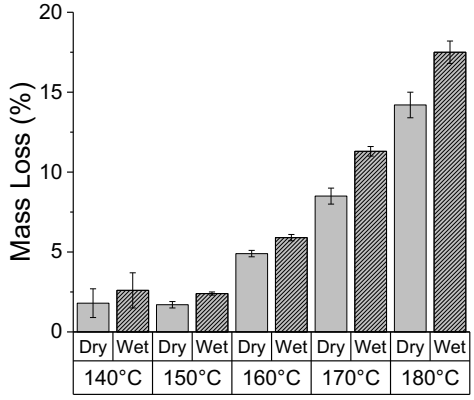


Figure 12: *Mass losses after the modification with different temperature with equivalent saturated steam pressure.*

5.1.4 Effect of relative humidity

The testing of the reactor was continued with changing the relative humidity in the treatment instead of the temperature. The purpose of this test was to see if the reactor works properly and the results are reliable. Based on the results of the previous measurement, two temperatures, 160 and 170 °C, were chosen for this test. Chosen temperatures where tested at five different RH: atmospheric RH, 25%, 50%, 75% and 100%. Atmospheric RH was 16% in 160 °C modification and 13% in 170 °C modification. Smaller RH was not possible in this experiment since vacuum would have been needed. The testing plan is demonstrated in Figure 13. Additional purpose of this test was also to see how the wood material behaves after the modification and therefore the samples were conditioned at 20 °C and RH 65% at the end.

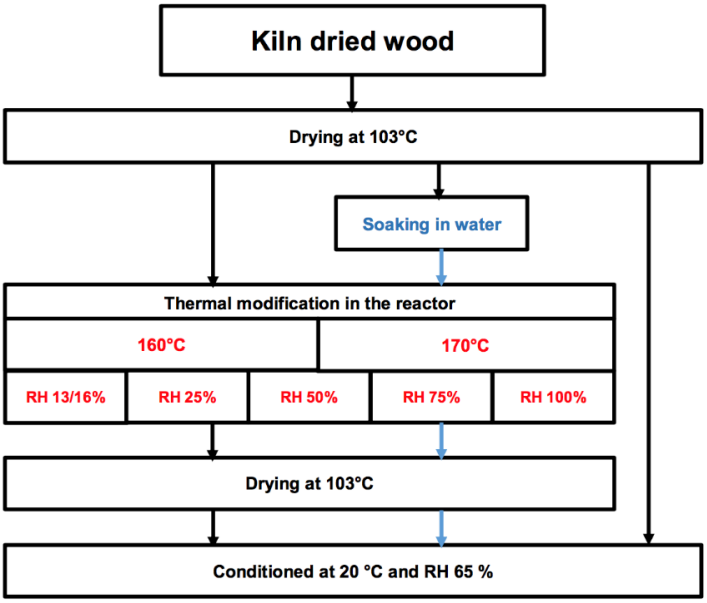


Figure 13: *Testing plan for relative humidity experiment.*

The desired RH was reached by changing the pressure in the reactor. Saturated vapour pressure was assumed to be same as RH 100% and based on that the other RH values were calculated from Equation 2 where X is the pressure set point in the reactor.

$$\mathrm{X\ (bars)} = \frac{\text{saturated vapour pressure (bars)} \cdot \text{target RH (\%)}}{100\ \%} \qquad \textbf{(2)}$$

Calculated pressures used as set points are in Table 2 in the left and right are the measured values. Thermal modification was done as described in section 5.1.3 with 15 dry samples and 15 wet samples. The treatment time was again 3 hours. Samples were dried afterwards at 103 °C for 24 h and the mass loss was calculated using Equation 1.

Table 2: *Set values and measured values for the process.*

Temperature (°C)	Pressure (bar)	RH (%)	Temperature (°C)	Pressure (bar)	RH (%)
160	1,01	16	158	1,08	18
	1,55	25	154	1,55	29
	3,09	50	156	3,07	55
	4,64	75	159	4,53	75
	6,18	100	162	6,09	94
170	1,01	13	165	1,08	15
	1,98	25	161	1,97	31
	3,96	50	165	3,9	56
	5,94	75	168	5,9	78
	7,92	100	172	7,73	93

Measured values differed slightly from the set values as can be seen from Table 2. Pressure stayed quite well in the range of set values and greatest variation was seen at RH 100%. Also, the temperature stayed quite well with only minor variations. Real RH is calculated in the right of the table based on measured values and is higher than set value for RH under 75% and lower for set values of 100%.

5.1.5 EMC measurement

After the treatment, samples were conditioned at 20 °C and RH 65%. The weight was measured after a week and then every two days until the difference between measured weights was less than 0.05 %. EMC was calculated based on the oven-dry mass and the mass after the equilibrium was reached.

5.2 Developing of the DVS analysis

This section focuses on developing the method for measuring hornification. In the literature review, the DVS method was valuated to be the best method to estimate accessibility of the hydroxyl groups in solid wood. Accessibility and its relation to hornification was also explained. The DVS apparatus (DVS Elevated Temperature ET, Surface Measurement Systems Ltd., London, UK) used in the tests is demonstrated in Figure 14. The sample is placed on the sample holder which is connected to ultra-sensitive microbalance. The RH in the chamber is maintained with flow of dry nitrogen gas which is mixed with water vapour or D_2O.

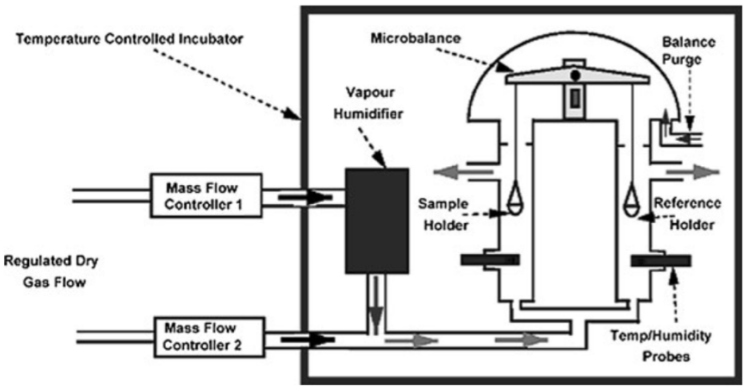
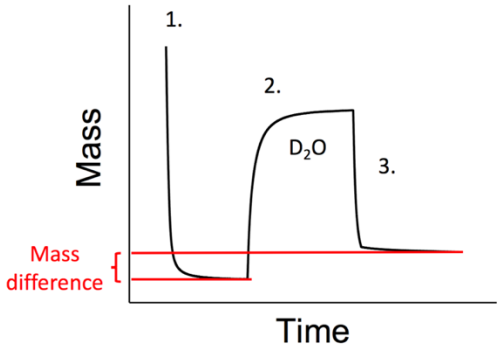


Figure 14: *DVS ET apparatus (Hill et al. 2010).*

Rautkari *et al.* (2013) and Kymäläinen *et al.* (2015) have used the method in their research for measuring accessibility in modified wood. In test performed by Rautkari *et al.* (2013), 10–20 mg of wood sample was placed in DVS apparatus and dried first with nitrogen. The equilibrium in all the steps was achieved when the mass of the sample was

changing less than 0.002% per minute (d*m*/d*t*) over 10 minutes. The example of the process is in Figure 15. Rautkari *et al.* (2013) used multiple deuteration steps but in the Figure 15 they are shown as one to simplify the figure. Multiple deuteration steps were concluded unnecessary in accessibility measurements by Pönni *et al.* (2014) and therefore they are not used in this thesis.



Stage	T (°C)	RH (%)	Liquid	Equilibrium
1. Initial drying	25	0	-	0.002% dm/dt for 10 min
2. D_2O impregnation	25	95	D_2O	0.002% dm/dt for 10 min
3. Drying	25	0	-	0.002% dm/dt for 10 min

Figure 15: *Method to measure accessibility modified from Rautkari et al. (2013a). The second step was multiple cycles in their work.*

The amount of accessible hydroxyl groups is calculated according the Equation 3 (Pönni *et al.* 2014).

$$A = \frac{(m_D - m_i)}{m_i} \cdot 1000 \frac{mol}{kg} \quad (3)$$

where A is the accessibility, m_i is the initial dry weight of the sample and m_D stands for the dry weight of the sample after deuterium exchange. The DVS method was developed in order to reach more reliable results and shorter treatment time (Pönni *et al.* 2014).

5.2.1 Inclusion compound

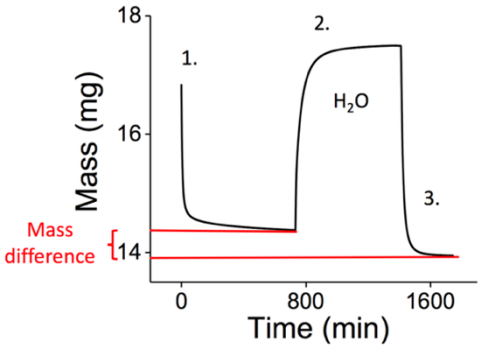
Hill *et al.* (2015) noticed that after the first drying step there was residual water trapped inside some of the samples. After re-wetting and second drying step, the trapped water disappeared. Therefore, if only first drying step is used, the accessibility results could be distorted by a residual compound. Based on these results, an additional test was performed with the hypothesis that there could be residual compounds in the samples after first drying. Term “inclusion compound” can be used to refer to the molecules

trapped in the wood sample after the first drying. Inclusion compound is noticed in cellulose research where it is used deliberately to increase the properties of the fibre derivates (Radu *et al.* 2013).

For this inclusion compound test, 20 mg of never-dried Scots pine samples were soaked in four different liquids: water, methanol, ethanol and 2-propanol. Samples were cut with a razor blade and then soaked in the liquids for 48 hours prior to testing. Drying was done with DVS (DVS Intrinsic, Surface Measurement Systems Ltd., London, UK) using nitrogen. Only H_2O can be used as a liquid in the DVS apparatus used in this section and therefore it differs from the one presented in section 5.2. Initial drying, as well as other stages, were done until the sample weight change was less than 0,0005 % per minute (d*m*/d*t*) for 10 minutes. After the drying, sample was moistened with water and then dried again. Inclusion compound was calculated with Equation 4.

$$\mathrm{IC} = \frac{(\mathrm{m} - \mathrm{m}_i)}{\mathrm{m}_i} \cdot 1000 \ \frac{\mathrm{mol}}{kg} \qquad \textbf{(4)}$$

where IC is the inclusion compound, m_i is the initial dry weight of the sample and m stands for the dry weight of the sample after second drying. Example of the method steps and measuring conditions are in Figure 16.



Stage	T (°C)	RH (%)	Liquid	Equilibrium
1. Initial drying	25	0	-	0.0005% dm/dt for 10 min
2. Water release	25	95	H_2O	0.0005% dm/dt for 10 min
3. Drying	25	0	-	0.0005% dm/dt for 10 min

Figure 16: *Example of the method for inclusion compound testing. Ethanol was used in this test as a liquid.*

Inclusion compound results for the four liquids are in Figure 17a. Water hardly had any inclusion compound and the effect to the results of accessibility would be minor.

Methanol had a bit more IC, still less than 1 %. However, ethanol had already a significant amount of IC, a bit over 3 % and 2-propanol even twice as much, around 6 %. The properties of the liquids are compared in Figure 17b to explain this results. 2-propanol has the greatest number of atoms, chemical bonds and highest molar mass whereas water has the lowest values in these three properties. Ethanol and methanol are in the between with methanol being closer to values of water.

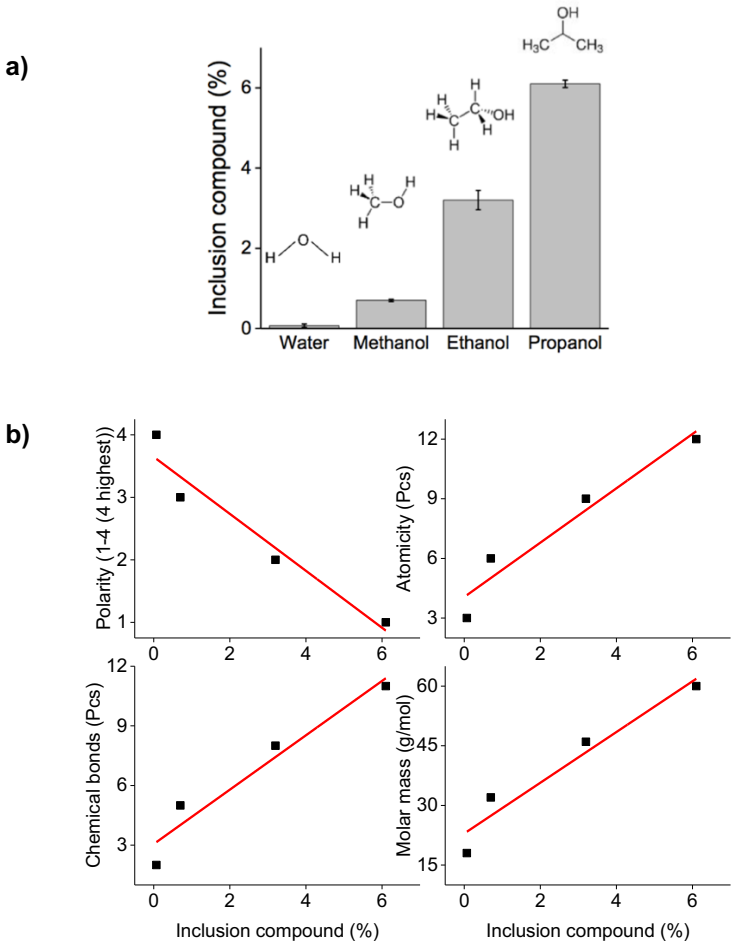


Figure 17: a) *Inclusion compound results.* ***b)*** *Comparing the results to the properties of the water, ethanol, methanol and 2-propanol.* R^2 *in all the curves is 0.94094.*

The result show clearly that the bigger the molecules of the liquid are, the more is trapped inside the wood sample during the first drying step. With ethanol and 2-propanol, the inclusion compound could affect significantly to the accessibility results. Besides, inclusion compound could disturb the results of the accessibility of hydroxyl groups since the compounds can prevent the change of the hydroxyl groups to deuterium groups. Therefore, an initial drying and moisturizing stage should be added to the accessibility measurement with DVS to eliminated the effect of inclusion compound. The suggested

steps were used in next test described in section 5.2.2 and the process can be seen from Figure 19.

5.2.2 D_2O impregnation time

One disadvantage of the DVS method used for hydroxyl accessibility measurements is the long duration of one measurement. Exposure time to D_2O is critical since it is the longest step in the process but it also greatly affects the accessibility results. (Pönni *et al.* 2014) This test was done to estimate the ideal time for D_2O impregnation. 10 mg pine wood samples were dried with the DVS from section 5.2 and the impregnation time for 95% RH with deuterium oxide was started with 2 hours and then increased up to 14 hours. The accessibility was measured after the impregnation and mass gain calculated comparing the mass before and right after the D_2O impregnation. The results for the accessibility are in Figure 18a and for the mass gain in Figure 18b.

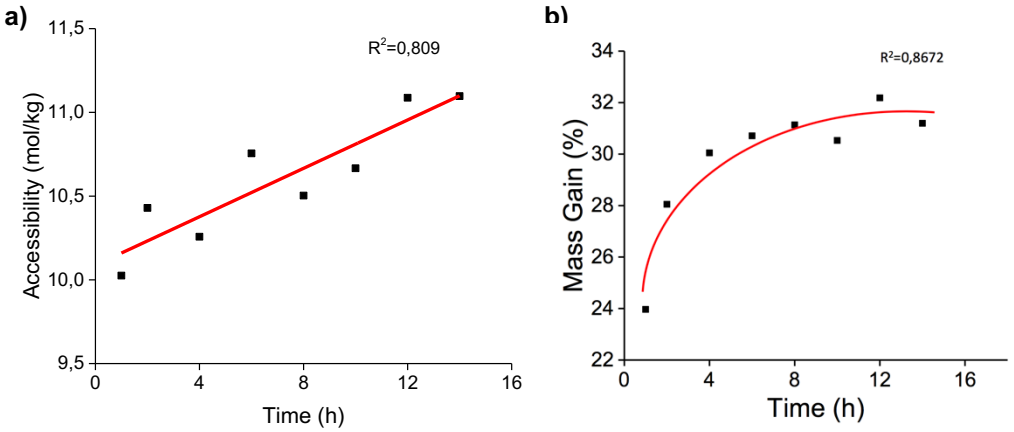
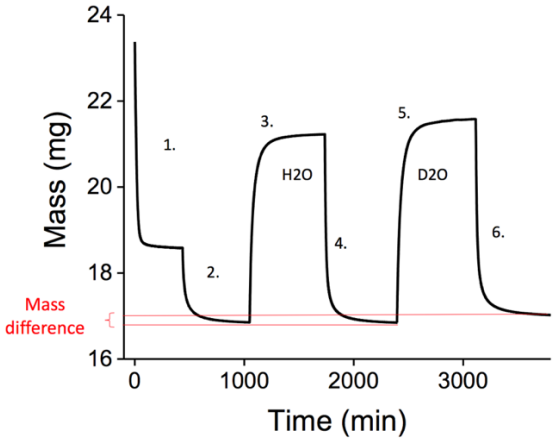


Figure 18: a) *Accessibility of hydroxyl groups depending on the deuteration time.* ***b)*** *Mass gain depending on the deuteration time.*

Hydroxyl group accessibility increased with increased deuteration time. This indicates that D_2O impregnation was not completed even after 14 hours. The experiment should have been continued to see how much further the accessibility would have increased. However, the mass gain stabilized after approximately 10 hours. Therefore, it could be assumed that accessibility would not increase long after that. Based on the results the deuteration time should be a bit over 10 hours and for example in 12 hours the D_2O impregnation could be assumed to be completed. The results are quite long compared to literature where deuteration of cellulose has been stated to be completed from 2 hour to several hours (Hishikawa *et al.* 1999). Still, the results from this test are used in the further experiments and deuteration time is set to 12 hours.

5.2.3 Hornification in initial drying

The impact of the initial drying conditions to hornification of wood were tested with DVS deuterium exchange method to find the suitable drying parameters for the main experiment. Green wood samples of 20 mg were set in the DVS apparatus described in the beginning of section 5.2. Example of the process steps used in the measurements are in Figure 19. Initial drying conditions where changed between four temperatures (25, 50, 75, 100 °C) and four relative humidity values (0, 25, 50, 95%) to find out how hornification depends on temperature and RH. Accessibility of the hydroxyl groups was measured right after initial drying and calculated with Equation 3.



Stage	T (°C)	RH (%)	Liquid	Equilibrium
1. Initial drying	50	50	-	0.0005% dm/dt for 10 minutes
2. Drying	25	0	-	0.0005% dm/dt for 10 minutes
3. Water release	25	95	H_2O	0.0005% dm/dt for 10 minutes
4. Drying	25	0	-	0.0005% dm/dt for 10 minutes
5. D_2O impregnation	25	95	D_2O	12 hours
6. Drying	25	0	-	12 hours

Figure 19: *Example of the new method to measure accessibility and initial drying at 50°C and RH 50%.*

In this test, process diagrams looked slightly different in the 1. and 2. stage depending on the initial drying conditions. In Figure 20a, where the initial drying was done at 0% RH and 100 °C, the mass dropped lowest in the stage 1 and increases in stage 2. The reason for this is in the fact that warm air rises and lifts the sample holder up making the sample seem lighter than it truly is. On the contrary, Figure 20b shows initial drying at 25 °C and 50% RH, and the weight did not decrease as much in stage 1 as in stage 2. This indicates that the sample did not dry completely during the initial drying. Therefore, stage 2 was initially added in the method to make sure that samples are dried after the initial drying.

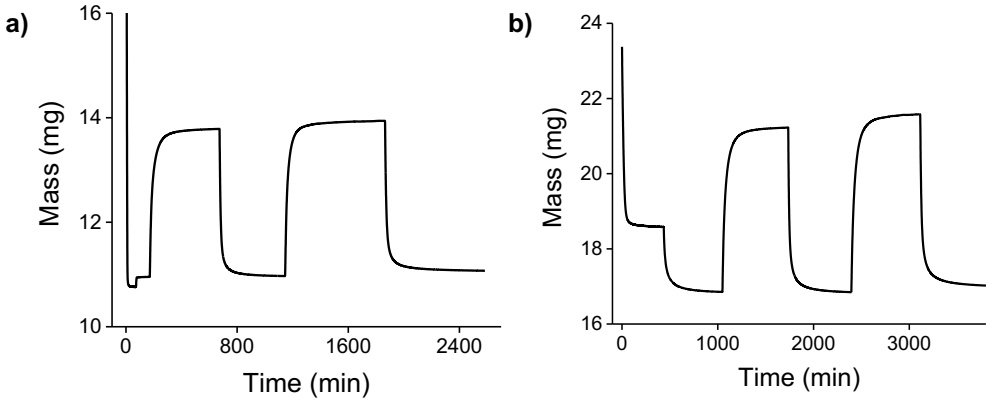


Figure 20: *Different process diagrams:* ***a)*** *initial drying at 100 °C and RH 0%* ***b)*** *initial drying at 25 °C and RH 50%.*

Example results for this initial drying test are in Figure 21a with RH changing and in Figure 21b with temperature changing. Based on the results, the drying temperature did not affect accessibility of hydroxyl groups when it stayed under 100 °C whereas the relative humidity had an effect. With increasing RH, higher accessibility was reached. This indicates that based on this test hornification is favoured in drying with lower RH values.

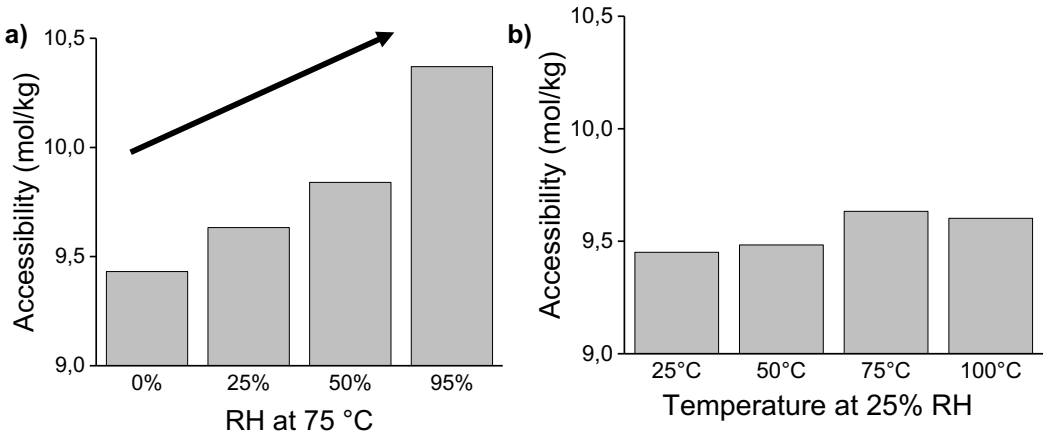


Figure 21: ***a)*** *Accessibility depending on initial drying temperature.* ***b)*** *Accessibility depending only from RH.*

The results got from this experiment were quite the opposite to a similar experiment executed by Suchy *et al.* (2010a). They found that temperature had an effect to the extent of hornification and initial drying at 25 °C resulted to considerably lower accessibility than initial drying at 80 °C. In their experiment, the RH did not have an effect to accessibility when dried at 25 °C but at 80 °C higher RH increased the accessibility. The differences between the results of Suchy *et al.* (2010a) and the experiment done in this thesis can

be explained with different method used and with small sample size. Suchy *et al.* (2010a) made the measurement with deuteration combined with FT-IR and they also used deuterium oxide in the initial drying. They also tested only one sample per each treatment as was done in the test with DVS. The number of simultaneous samples should be increased to get reliable results. Once again, the results from the test done in this thesis are used for the further experiments.

5.3 Effect of hornification on the properties of thermally modified wood

The purpose of this section was to modify wood in high-pressure reactor under saturated steam and dry it under five different conditions after the modification. The EMC, mechanical properties and swelling properties were measured, and hornification estimated with DVS to see if it affected to the properties. The testing plan is in the Figure 22 where the experiment is connected to the preliminary tests with the reactor and the DVS. Chemical analyses are explained in section 5.4.

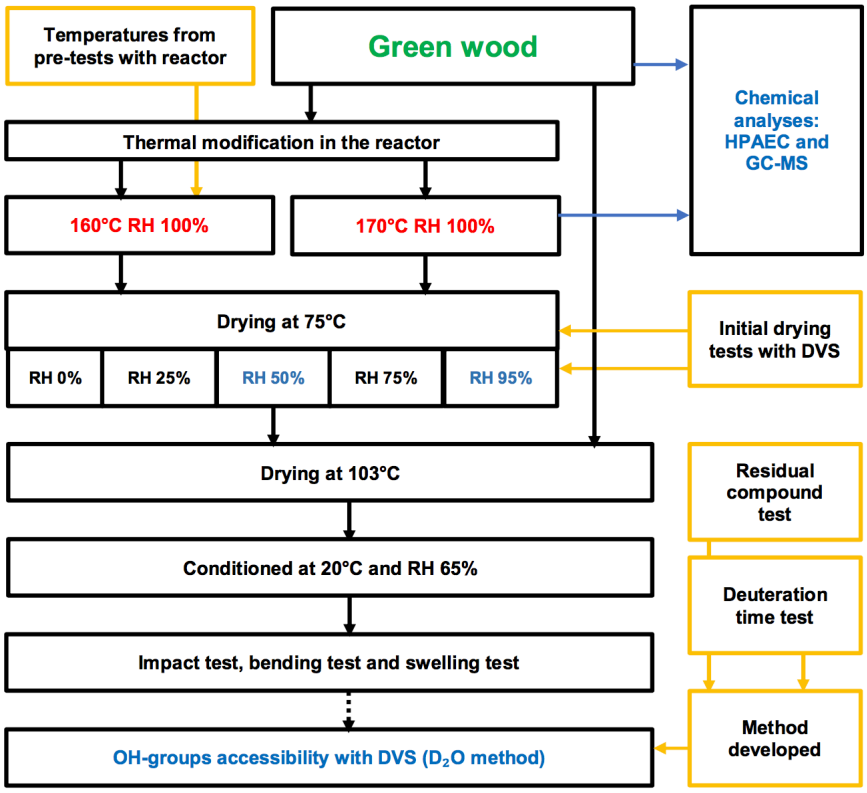


Figure 22: *Testing plan for the effects of hornification to the properties of thermally modified green wood.*

5.3.1 Material information

Scots pine (*Pinus sylvestris L.*) boards were used in this experiment. Never-dried green wood boards were provided by Versowood in Vierumäki and only sapwood boards were chosen. The material cutting plan is demonstrated in Figure X. After step 1, the pieces of the boards were kept in a freezer and cut on the day of modification to sample dimensions of 14 cm longitudinal, 1.5 cm radial and 1.5 cm tangential as showed in step 3. MC sample pieces were cut from every fifth sample, weighted and dried at 103 °C for 24 hours for MC determination. MC value was used to estimate the initial weight of the samples and based on that the mass loss was calculated using Equation 1. After the modification and initial drying, samples were dried at 103 °C for 24 hours and then conditioned at 20 °C and RH 65%. After EMC was reached as described in section 5.1.5, the samples were cut and planed to pieces of required dimensions for bending test (Figure 24a), impact test and swelling test (Figure 24b).

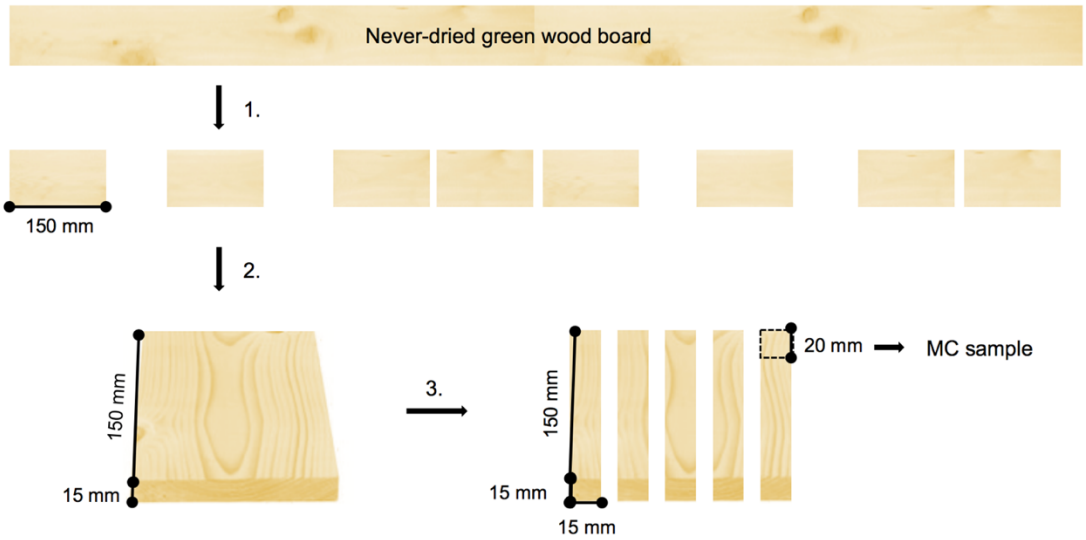


Figure 23: *Material cutting plan for green wood board. 1) Knots and cracks are eliminated. 2) Material is kept in a freezer and cut just before going to the reactor. 3) Material is cut to pieces that go in to reactor but before that small MC sample is taken.*

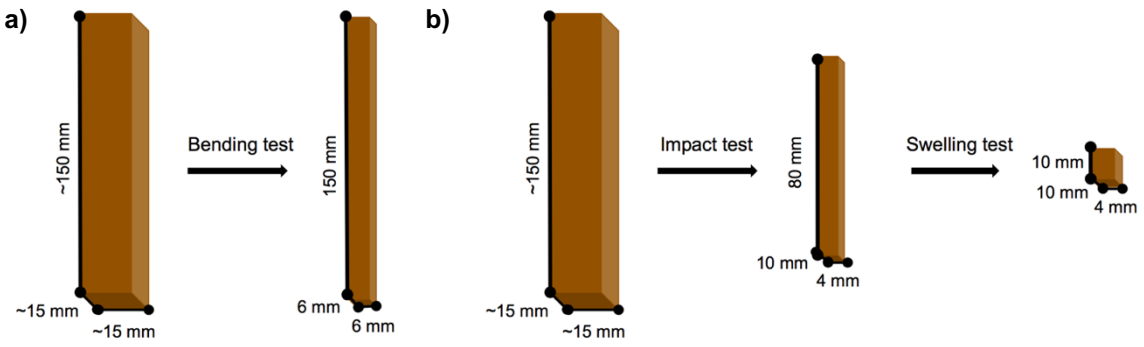


Figure 24: *Material cutting plan after the thermal modification.*

5.3.2 Thermal modification and drying

Green wood samples were thermally modified under saturated vapour pressure and for 3 hours with the high-pressure reactor described in section 5.1.1. Two different temperatures, 160 and 170 °C, were used based on the test explained in section 5.1.3. Immediately after the treatment, samples were dried in air-and-steam oven (Electrolux) at 75 °C. Five different relative humidity values were used: 0, 25, 50, 75 and 95%. Samples were dried for 6 hours at each RH.

5.3.3 Accessibility of the hydroxyl groups

Accessibility was measured with the DVS apparatus introduced in section 5.2. The method used was the same as in section 5.2.3 but temperature in initial drying was kept at 25 °C and RH 0%. DVS measurement was done for two treatments thermally modified at 160 °C, drying at RH 50% and RH 100%. Also, unmodified samples were used as a reference. Measurement was done in duplicates for each treatment.

5.3.4 Bending test

Bending test for wood boards is usually done according the standard EN 408 (2011). EN 408 is a 4-point bending standard for static modulus of elasticity (MOE) and modulus of rupture (MOR) for timber structures but the minimum length described by the standard was too long for the samples treated in the high-pressure reactor. Therefore, 3-point bending modified from EN 310 (1993) was used. Sample size was 13 cm x 0.5 cm x 0.5 cm. The test was carried out with Zwick testing apparatus (MTS Renewal, Zwick, Germany) equipped with bending test spans. The distance between the supports was 10 cm. MOE and MOR were calculated according the standard (EN 310 1993).

5.3.5 Charpy impact test

Charpy impact test was done following the EN ISO 179-1 (2010) made for testing of plastics. Samples were treated as long-fibre-reinforced material and conditioned 24 hours in the testing room according to standard. Test was done with Charpy impact testing machine (HIT5, Zwick, Germany) for un-notched samples and flatwise impact was tested in parallel-to-fibre direction. Sample dimensions of 8 cm (length), 1 cm (width) and 0.4 cm (thickness) specified by the standard were used. The span in the machine was 6.2 cm and pendulum of 4 J was used. The un-notched Charpy impact strength was calculated according the standard (EN ISO 179-1 2010).

5.3.6 Swelling test

The swelling test was done with samples of 1 cm longitudinal, 1 cm radial and 0.5 cm tangential sawn from the impact test pieces. Five samples of each treatment were used. Samples were dried at 103°C for 24 hours prior to the test and their dimensions were measured with a slide caliper. Samples were then placed in deionized water for a week and measured again. Swelling and ASE values were calculated following the equations from Hill (2006, pp. 33-34).

5.4 Chemical analysis

Chemical analyses were done to the acetone soluble compounds from unmodified wood and thermally modified wood, and to the residual water coming from the thermal modification. The aim of this experiment was to understand more about chemical reactions that occurs in this specific process and whether it can be related to those reported in literature. The main analysis used here was gas chromatography-mass spectrometry (GC-MS) but also high performance anion exchange chromatography (HPAEC) was performed to residual water.

5.4.1 Sample preparation

Same material was used as described in section 5.3.1. Green wood samples were thermally modified in high-pressure reactor for 3 hours at 170 °C under saturated steam pressure. The samples were then dried with unmodified samples at 103 °C for 24 hours and milled to 60 mesh. Extraction was done to unmodified and modified samples as duplicates. 5 g of milled wood was weighted to each Soxhlet sock and extracted for 6 hours with acetone (Sigma-Aldrich, 98.7%). The acetone was then evaporated from the samples by leaving the solution in the fume hood for two days.

After the thermal modification, there was about 1 litre of liquid on the bottom of the reactor. The liquid was weighted and then two 20 ml samples were taken from it. The pH values of those samples were measured three times with Thermo Scientific pH meter (Thermo Scientific Orion 2-star benchtop pH meter, USA) and the average calculated. The solution was then filtered with Whatman Glass microfiber filters (Grade GF/F, Whatman plc, UK). After that the other 20 ml sample was saved for the HPAEC test and other was was placed in a freeze-drying holder and kept in the freezer over-night. Sample was then freeze-dried with Labconco freeze-drier (Labconco Corporation MO 64132, Kansas City, USA) for 20 hours.

5.4.2 HPAEC

Monosaccharides in the residual water sample were determined with HPAEC equipped with CarboPac PA20 (ICS-3000, Dionex Corp., Sunnyvale, CA, USA). Filtered sample was diluted to 100 with Mill-Q prior to the analyse. The analysis was performed by the technical staff in Aalto University School of Chemical Engineering.

5.4.3 GC-MS

Individual components in the condensation water samples and acetone soluble compounds from the modified and unmodified samples were aimed to identify using GC-MS. Dried residual water samples were diluted to one tenth and extractives to one hundredth with pyridine (Aldrich, 98%). All three samples were run as duplicates. 1 mg of diluted samples were mixed with 0.5 ml of pyridine and 0.25 ml of solution of BSTFA with 5 % TMCS. Samples were placed to a single quadrupole mass spectrometer (Thermo Scientific ISQ series, USA) coupled with gas chromatograph (Trace 1300). Measurement was done with 30 m x 250 µm x 0.25 µm i.d. column (TraceGOLD TG-200MS) and helium used as the carrier gas (1.2 ml/min).

6 RESULTS AND DISCUSSION

The aim of this Chapter is to review and analyse the results from Chapter 5. Results are compared to literature and critically discussed. The Chapter is divided into three parts and first the focus is in the results of the pre-test with changing RH. Then the experiment of hornification effecting to the properties of thermally modified wood under saturated steam is reviewed and discussed. Last, the results from chemical analyses are compared to the literature.

6.1 Results from the relative humidity experiment

This test was performed to learn more about the high-pressure reactor and how the material behaves after different treatments performed with the reactor. The results for 160 °C modifications are in Figure 25a, b and for 170 °C in Figure 25c, d. Most of the results are logical, supporting the theory that increasing RH increases the mass loss. Soaked samples result in greater mass loss compared to dry ones. The mass loss should be at least 3% to improve dimensional stability (Viitaniemi *et al.* 1997). Only 75% and 95% at 160 °C reach the requirement, and at 170 °C starting from RH 50%.

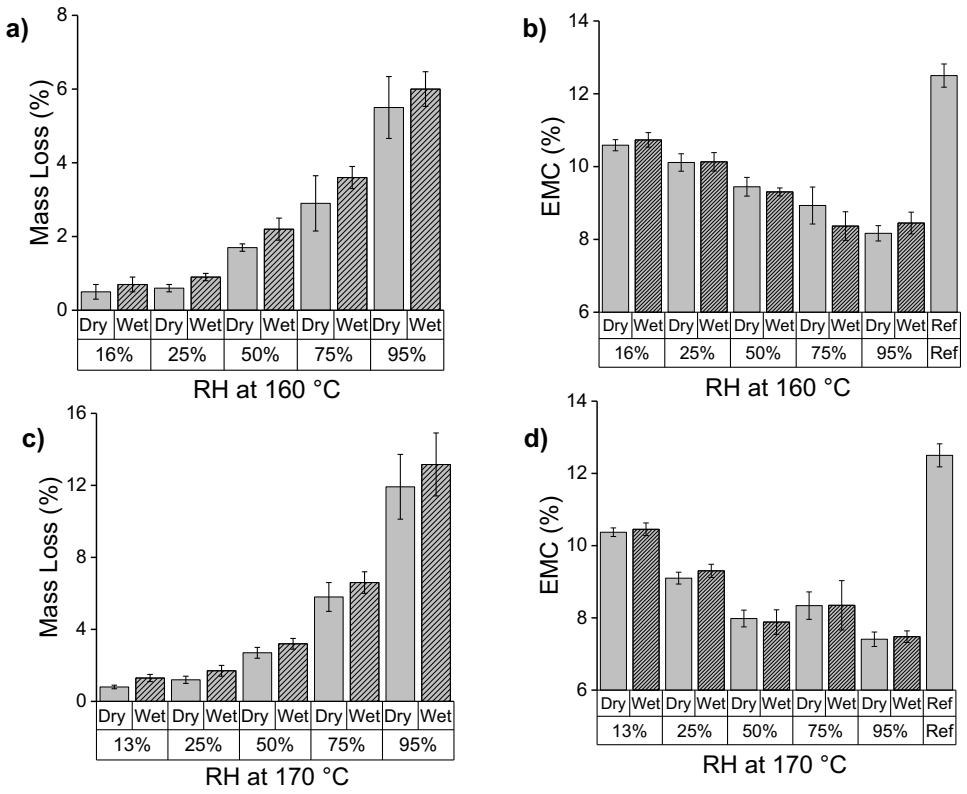


Figure 25: a) *Mass loss* ***b)*** *EMC after thermal modification at 160 °C with different relative humidity.* ***c)*** *Mass loss* ***d)*** *EMC thermal modification at 170 °C with different relative humidity.*

The standard deviation of the mass loss in both Figure 25a and 25c increases as the relative humidity increases. For example, at 170 °C and RH 25%, the standard deviation is around 1% whereas in 170 °C and RH 95% it is already around 4%. This might be caused by the extractives and other degradation products that stay in the sample after the modification. The phenomenon increases with increased mass loss. (Altgen *et al.* 2016) This affects the results since the amount of these compounds is not standard. The disturbance could be avoided with corrected mass loss measurement where the sample is extracted before the mass loss measurement. (Altgen *et al.* 2016)

The EMC and mass loss is compared in Figure 26 and it can be concluded that EMC is somewhat inversely proportional to the mass loss. The same have been proven earlier (Altgen and Militz 2016). However, noticeable is that EMC of the wet and dry samples are quite the same at the same relative humidity even though the mass loss differs. This is clear for example at 170 °C RH 95%, where the mass loss is around 2% higher in wet samples but the EMC is still same for wet and dry samples. This indicates that the mass loss is not the only mechanism effecting the EMC. Altgen and Militz (2016) noticed that

initially wet samples act differently after thermal modification than initially dry samples. In their experiment, the dimensional stability of wet samples decreased with increasing mass loss whereas in dry samples the dimensional stability is directly proportional to the mass loss. Same can be seen in this results from 160 °C and 95% RH modification where wet samples have 0.5% higher EMC compared to dry samples.

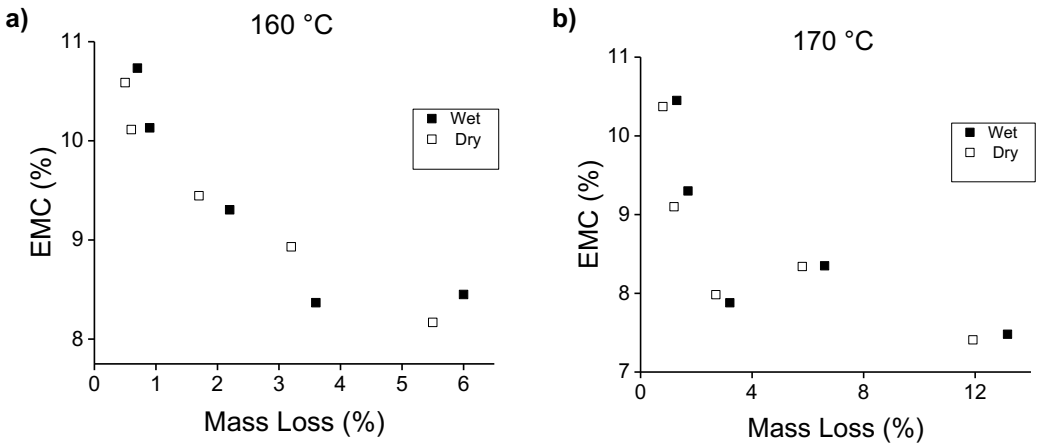


Figure 26: *Correlation of mass loss and EMC a) modified at 160 °C, b) modified at 170 °C.*

6.2 Effect of hornification on the properties of thermally modified wood

The aim of this experiment was to investigate the effects of hornification on the properties of wood thermally modified under saturated steam. The assumption was that during the modification no hornification occurs, and therefore, the extent of hornification could be defined in the drying step after the modification. Based on the experiment in section 5.2.3, hornification was expected to decrease with increased RH in drying. To estimate the extent of hornification, equilibrium moisture content (EMC) and accessibility of the hydroxyl groups were measured. Mechanical properties and swelling properties were tested to evaluate whether hornification affects any of those.

6.2.1 EMC

The mass loss was assumed to be the same, around 6%, between the samples thermally modified at 160 °C, and around 12% at 170 °C. The only difference was the drying conditions after the thermal modification. EMC values for both modifications can be seen from Figure 27a and 27b. The results in Figure 27a are differing between the drying conditions but at 170 °C, no differences can be seen from the figure.

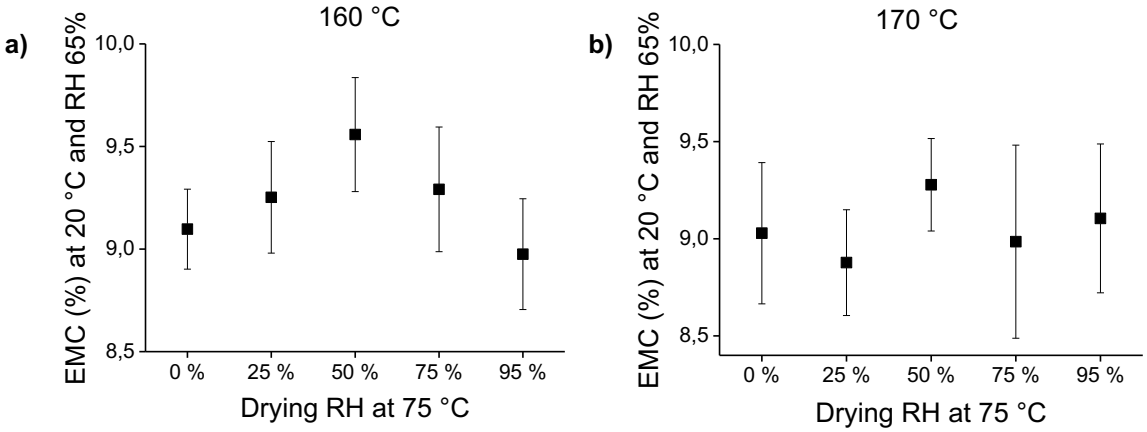


Figure 27: *EMC at 20 °C and 65% RH for samples thermally modified at* ***a)*** *160 °C* ***b)*** *170 °C and dried differently.*

Statistical analysis was performed to the results of EMC to find out the significant of the variations. Minitab program (Minitab 17, Minitab Inc.) was used as an analysis tool and one-way variance analyse (ANOVA) was drawn with 95% confidence interval (CI). Example of the analysis is in Figure 28 where the dependence of EMC on the drying RH is analysed. Statistical difference is detected based on the overlaps of the CI vertical bar. For example, drying at RH 95%, 25% and 75% had no statistical difference in EMC since the CI vertical bars are clearly overlapping. However, drying at RH 0 % and 50 % have statistically significant differences in EMC since the CI vertical bars are not overlapping at all.

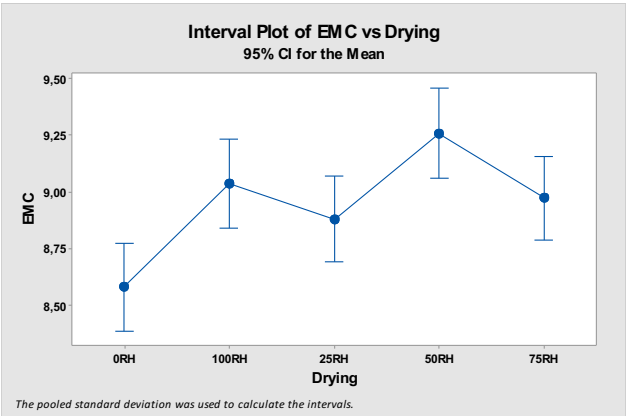


Figure 28: *ANOVA analysis done for samples thermally modified at 160 °C and dried at different relative humidity.*

Based on the ANOVA analysis, there was a notable difference in the EMC values of 160 °C. Therefore, it could be stated that the drying method affected to the EMC. EMC is strongly connected to the accessibility of the OH-groups in the sample since they are

responsible for adsorbing the moisture from the surroundings. Based on that, hornification could be assumed to be greatest in the samples dried at RH 95% or RH 0% and lowest in the sample dried at RH 50%. This is disagreeing with the results from initial drying test done in section 5.2.3 where the lowest hornification was achieved with the highest RH. Since the initial drying test with DVS was done only for one specimen in each condition, it is not reliable. These EMC tests were done for 20 samples each so they are more likely to give precise results. Furthermore, the result with least hornification at RH 50% is logical if the hornification is dependent on the severity of the drying. In this experiment, with the 95% RH drying the sample stayed quite saturated and was then dried at RH 0% and 103 °C. This is considerably more severe drying than starting with RH 50% where the sample already dries some and is then dried completely at RH 0%. The theory is supported by the fact the RH 0% initial drying and RH 95% initial drying resulted to quite similar EMC.

Nevertheless, there was no differences between the 170 °C modification based on the ANOVA analysis and the Figure 27b. One reason for this is that he standard deviations in the 170 °C results, especially in the RH 75% drying, are quite significant and therefore no differences can be stated. Also, the mass loss is relatively high at the 170 °C treatment which might prevent the hornification from occurring if the hydroxyl groups are not in contact with each other due to the massive degradation. Based on these results, the accessibility measurement where outlined to samples thermally modified at 160 °C and dried at RH 50% and 95%.

6.2.2 Accessibility of the hydroxyl groups

Results from the hydroxyl groups accessibility measured with DVS are in Figure 29. The results were, as expected, based on the EMC measurement, and drying at RH 50% resulted in lower hornification than the drying at RH 95%. Therefore, the assumption that the state of hornification can be estimated based on EMC was presumably right. Also, it seems that the drying RH had effect on the hornification and it was favoured in severe drying, from which the RH 95% is an example as explained in section 6.2.1. However, these tests were carried out only twice and they should be repeated to get reliable results. Besides, the variation in 95% drying is quite high which also decreases the reliability of this results. Unpredictably, the accessibility difference between the RH 50% sample and references sample was quite low.

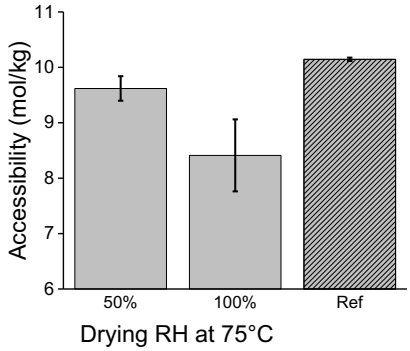


Figure 29: *Accessibility of hydroxyl groups after the 160 °C modification and drying at 75 °C with RH of 50% and 95%. Unmodified sample was used as a reference.*

6.2.3 Mechanical and swelling properties

Impact strength, MOE and MOR were tested from the samples and mechanical properties were evaluated based these tests. Also, the water-uptake was tested and swelling and ASE calculated to learn more about the moisture behaviour of the samples. Results from these tests are summarized in Table 3. In Appendices 1 and 2 the same results are presented visually. ANOVA analysis described on section 6.2.1 was done for the results and they are in Appendix 3. For swelling and ASE values, the ANOVA analysis was not performed due to the small number of simultaneous samples.

Table 3: *Results from impact test, bending test and swelling test for samples dried differently after 160 °C or 170 °C thermal modification in saturated steam.*

Modification	Drying RH (%)	Impact strength (kJ/m^2)	MOE (kN/mm^2)	MOR (N/mm^2)	Swelling (%)	ASE (%)
Reference	-	34.3 (6.1)	11.9 (1.9)	100.2 (11.3)	18.5 (1.6)	-
SA 160 °C	0	20.8 (7.1)	12.0 (0.9)	71.9 (11.5)	15.0 (3.4)	18.6
	25	12.3 (2.8)	8.7 (1.4)	51.6 (10.2)	15.1 (3.1)	18.4
	50	22.8 (6.5)	12.3 (0.8)	84.3 (11.1)	14.6 (1.4)	20.1
	75	18.7 (5.8)	12.4 (1.4)	75.0 (12.4)	15.8 (0.9)	14.7
	95	19.0 (4.5)	11.7 (1.1)	75.1 (11.0)	15.5 (2.4)	16.1
SA 170 °C	0	8.7 (2.4)	9.3 (1.1)	46.6 (8.5)	12.5 (1.3)	32.4
	25	9.4 (2.1)	9.6 (0.8)	53.3 (10.6)	13.5 (2.7)	28.2
	50	8.6 (1.3)	9.0 (0.8)	42.9 (6.8)	12.3 (4.6)	33.3
	75	10.4 (2.6)	9.7 (1.2)	42.9 (7.6)	14.0 (0.9)	24.5
	95	11.1 (4.9)	9.9 (1.3)	51.0 (9.4)	14.9 (1.3)	19.1

Based on the ANOVA analysis, there are statistical differences in the MOE and MOR values of RH 25% drying compared to other drying RHs at the 160 °C modification. 25% RH drying resulted in significantly lower values in the bending test maybe due to the

possibility that material used for this test might have contained cracks that are not visible. Also in the 170 °C modification, there was remote differences between the MOR values of 25% RH drying and 50% RH drying but the opposite way as at 160 °C modification. However, none of the other properties differed from each other statistically. Therefore, these few differences are more likely to be measuring or protocol mistakes. These results are not connected to the hornification at all. The assumption was that differences could be seen in the 160 °C modification between drying at RH 50% and RH 95%. The average results for impact strength of RH 95% are 2 kJ/m^2 lower than the average of RH 50%. But based on the ANOVA analysis, this difference is insignificant. Therefore, it is concluded that based on the results, hornification had no effect on the mechanical or on the swelling properties of thermally modified wood.

Even though hornification had no effect to the properties in this experiment, the reality can still be different. The accuracy of these results had to be estimated. The results from the swelling test should be looked critically since they are not reliable due to the small number of simultaneous samples. However, the swelling values for the reference sample and for the modified samples are in the same range as in the similar experiment performed by Rautkari *et al.* (2014). The impact strength is relatively high in 160 °C modification compared to the results of Rautkari *et al.* (2014) where it was around 9 kJ/m^2 for 150 °C saturated modification. The 170 °C impact strength values are in that range despite the mass loss being about 5 times higher than in 150 °C modification in the article. Ding *et al.* (2011b) found impact strength of 21.7 kJ/m^2 for sample modified at 200 °C under pressurized steam for 2 hours. This is quite close to the values of 160 °C modification found in this experiment.

MOE values are significantly lower in this experiment than in Rautkari *et al.* (2014) experiment. They had MOE around 16 kN/mm^2 with 180 °C saturated modification whereas in this experiment even the 160 °C MOE values are under 12 kN/mm^2. However, MOE values tested by Ding *et al.* (2011b) at 200 °C under pressurized steam were average of 11.0 GPa which is relatively close to the values achieved here. The MOR results, on the other hand, were rather similar with the results of both Rautkari *et al.* (2014) and Ding *et al.* (2011b). The MOR values of the both articles were between the MOR values of 160 °C and 170 °C test. The differences in MOE can be explained with the different testing method since 4-point bending was used in the articles and 3-point bending in this experiment. Higher MOE values are reached when the force is applied from two points instead of one.

The measured values seem to be mostly in the right range when compared to literature. This is indicating that the testing was performed successfully. However, shortages in the testing method are found such as lack of specimens, especially in the swelling test, and too small sample size in the bending test. More tests should be performed to rule out the effect of assumed hornification completely from thermally modified wood.

6.3 Results from chemical analyses

The aim of the chemical analyses was to learn more what happens to the wood material during the thermal modification under saturated steam. Thermal modification for this test resulted in 11.68% mass loss and 1.2 litres condensation water came out of the reactor. The water was found to be quite acidic as the average pH value was 2.30.

Thermally modified wood was found to consist 4.7% of acetone soluble compounds and unmodified wood 3.4%. For unmodified wood the result is almost same as in literature for Scots pine which is 3.5% (Sixta 2006, s. 23). Ding *et al.* (2011b) found similar results to this experiment and the extract content for thermally modified wood in pressurized steam was around 3.5 % when the control sample had 2.8% extracts. Increase is then 25% in their experiment, while in this experiment it was 38%. The difference can be explained by the differences in the thermal modification since Ding *et al.* (2011b) used higher temperature but shorter time and lower steam pressure. Therefore, the treatment was milder.

6.3.1 HPAEC

The sugars of the condensation water solution where analysed with HPAEC. This test was not performed to the thermally modified and unmodified wood sample since there was good comparison values in the literature already (Sixta 2006, Karlsson *et al.* 2012). In Table 4 are the amount found molecules and their relative area and height. The amount (mg/l) is for 100 times diluted samples so in the real sample the amount 100 times more.

Table 4: *Results from HPAEC.*

Compound	Area (nC*min)	Height (nC)	Area (%)	Height (%)	Amount (mg/l)
Arabinose	3.7	7.4	10.4	17.6	175.0
Rhamnose	0.3	0.5	0.8	1.1	19.9
Galactose	3.8	6.0	10.6	14.2	141.7
Glucose	4.9	6.1	13.6	14.5	173.2
Xylose	9.3	10.0	25.9	23.8	345.8
Mannose	13.9	12.2	38.6	28.8	632.7
Total	36.0	42.3	100	100	1488.3

There was clearly most of mannose in the residual water with relative area of 39%. Next is xylose with 26% followed by glucose 14%, galactose and arabinose around 10% and rhamnose 0.8%. Arabinose and galactose are from the degradation of pine arabinogalactan (Esteves *et al.* 2011), and therefore, it is logical that they have same relative area, around 10%. Xylose is corresponding to the degradation of arabinoglucuronoxylan and mannose to galactoglucomannan (Esteves *et al.* 2011).

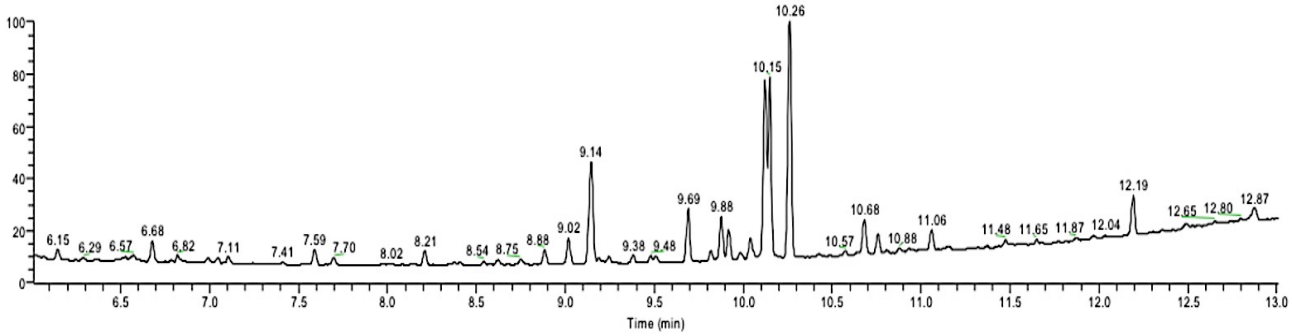
Based on the literature, there are 12.4% mannose, 7.6% xylose, 1.9% galactose and 1.5% arabinose in unmodified Scots pine (Sixta 2006). Karlsson *et al.* (2012) found that in pine wood treated at 170 °C in saturated steam mannose and galactose cover around 60% of the sugars. Other sugars were percentually around 30% glucose, 8% xylose and 0.3% arabinose in their experiment. In condensed water, mannose and galactose cover together around 50% of the sugars, which is slightly less than in modified wood. In unmodified wood, the amount of mannose and galactose, 14.4%, is significantly lower than in modified wood or in the condensed water. Also, there is less xylose and arabinose. These sugars are from hemicelluloses that degrades during the modification. Glucose, however, is more thermally stable since it is the component of cellulose that is not degrading. There is a lot more glucose in the modified sample than in the condensed water.

It can be concluded, that degradation compounds from hemicelluloses stay inside the high-pressure reactor based on the HPAEC results of condensed water and analysis of Karlsson *et al.* (2012). Some of the compounds, such as xylose and arabinose, are more likely to leach to the condensed water since their percentual share was greater in water than in modified sample. On the contrary, there is more mannose and galactose in the modified sample compared to condensed water. There was relatively high amount of sugars in the condensed water, and there could be a possibility to make the sugars a by-product.

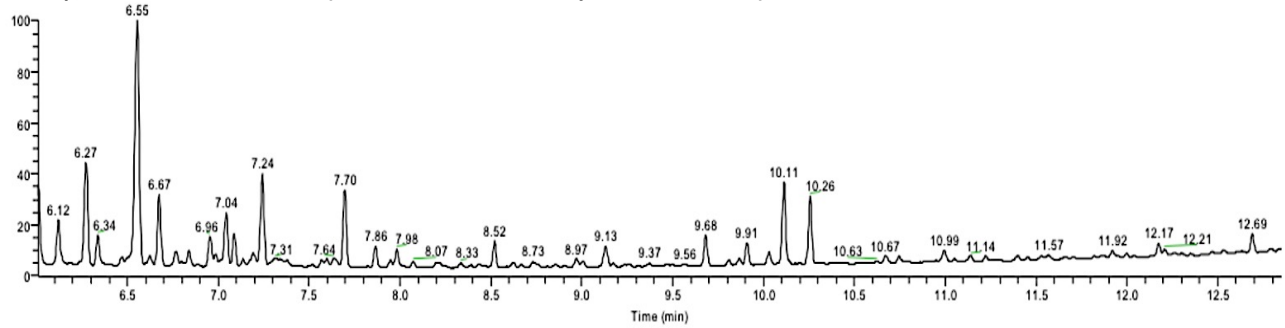
6.3.2 GC-MS

Gas chromatogram spectra for acetone soluble compounds from unmodified and thermally modified pine samples are in Figure 30a and 30b. GC-spectra from condensation water is in Figure 30c. There are clearly least peaks in unmodified sample and most peaks in the condensation water. Thermally modified and unmodified samples have some peaks in common, such as 10.26 and 9.14, but quite many differences also.

a) Acetone soluble compounds from unmodified sample



b) Acetone soluble compounds from thermally modified sample



c) Condensation water

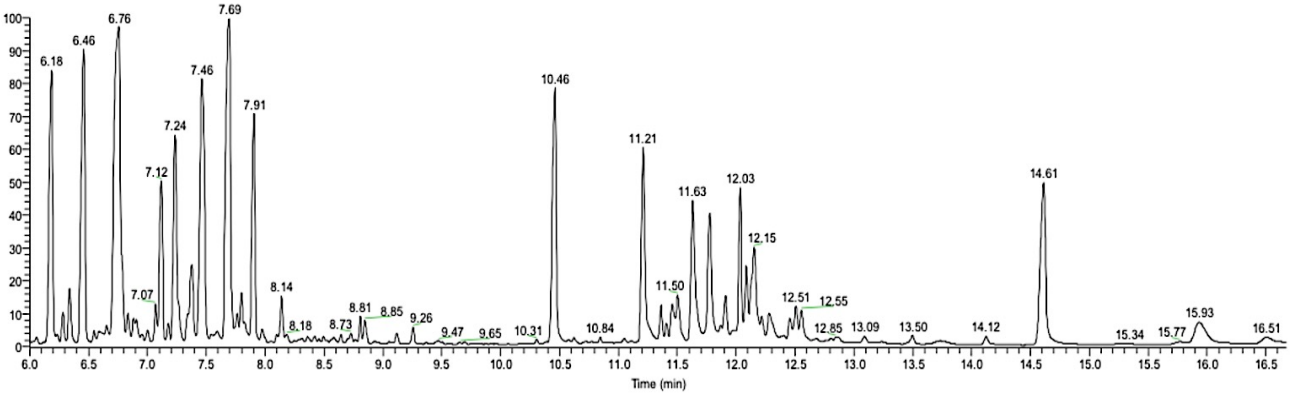


Figure 30: *Gas chromatograms spectra from acetone soluble compounds from* ***a)*** *unmodified wood* ***b)*** *thermally modified wood and* ***c)*** *condensation water. X-axial is the retention time in minutes and Y-axial is the relative abundance. Note: different scale in Figure c).*

Highest peaks of all the three GC-spectra were analysed by their MS spectra. MS spectra was compared to NIST-library (NIST MS Search 2.2) and the first five compound options from the library were compared. The probability was considered, but also the similarities in the spectra. Example of the spectra analyses can be seen from Figure 31 where the MS spectra of peak 6.8 from condensation water GC-spectra is compared to MS-spectra of D-Xylose. The probability for this was 30.9 %. As seen from the Figure 31, peaks 73, 147, 191, 204 and 217 are same and they have the same relation to each other in both the spectras.

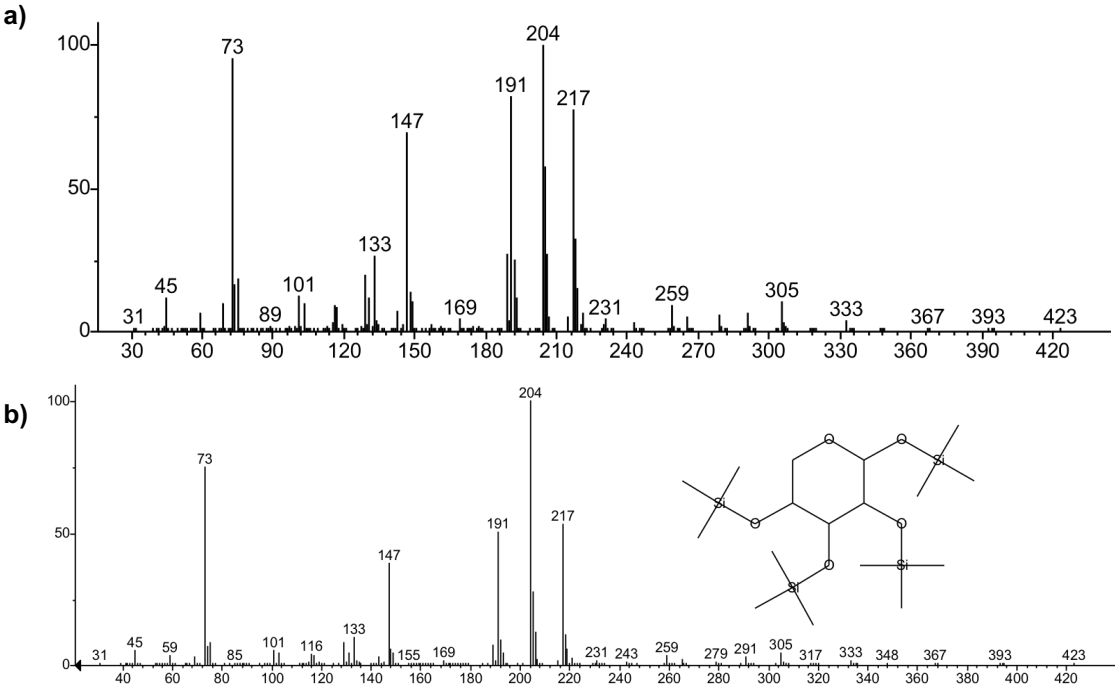


Figure 31: *Examples:* ***a)*** *MS spectra of peak 6.8 from GC-spectra of condensation water,* ***b)*** *MS spectra of D-Xylose.*

Results from GC spectras compared to MS spectras are in Appendix 4. Also, compounds probability is presented there. The only common compounds found from all three samples was vanillin and galactopyranose. Otherwise, the extractives from unmodified wood samples did not match to condensation water. However, extractives from thermally modified wood samples had more similarities with both the other samples. For example, pimaric acid, isopimaric acid, abietic acid, 9-octadecenoic acid and petroselic acid where found from both modified and unmodified samples. D-xylose, D-mannopyranose, D-talopyranose, D-glucopyranose, coniferyl aldehyde and lactone are found from condensation water and modified sample.

Galactopyranose, D-xylose and D-mannopyranose comes probably from polysaccharide pyrolysis, such as degradation of galactose, arabinose, xylose and mannose (Faix *et al.* 1991, Esteves *et al.* 2011). Therefore, it is logical to have more of those in the modified sample and condensation water. Levoglucosan was found only from modified sample and that is often considered as a degradation product of cellulose (Gao *et al.* 2003). This supports the suggestion made in the previous section, 6.3.1, that degradation products of cellulose are attached to the material rather than leaching to the condensation water. Besides hemicelluloses and cellulose, there are also compounds probably coming from the lignin pyrolysis, such as vanillin and coniferyl aldehyde (Faix *et al.* 1990). There are also different types of extractives commonly found from pine wood, such as pimaric acid, isopimaric acid, abietic acid and 9-octadecenoic acid (Sixta 2006, s. 33-37).

Based on the GC-MS analysis, it can be confirmed that there are significant amounts of degradation compounds and extractives in the high-pressure reactor after the modification. Some of those are in the condensed water but also great amount is in the modified sample. The extractives together with degradation compounds are likely to affect the mass of modified wood as suspected in the section 6.1. Also, if the extractives stay in the modified wood, they might have effect on the properties of the material. For example, many extractives are found to defend wood against fungal attack (Diouf *et al.* 2002, Amusant *et al.* 2007).

7 CONCLUSIONS

The aim of this thesis was to investigate the effect of hornification on the properties of Scots pine thermally modified under saturated steam. Therefore, a high-pressure reactor was introduced and based on the pre-tests, temperatures of 160 °C and 170 °C in saturated steam were chosen as process parameters. Hornification was tested using deuterium exchange method in DVS apparatus. The method was first tested and developed. Based on residual compound test, an additional re-wetting step was added to the testing method. Also, the impact of deuteration time was tested and 12 hours of deuteration was found to give reliable results. Initial drying test was carried out to see if temperature or relative humidity had any effect on the extent of hornification. Relative humidity was found to have an impact on hornification, and therefore, it was varied in the real experiment.

In the actual experiment, never-dried Scots pine samples were thermally modified at 160 °C and 170 °C under saturated steam for three hours. After the modification, samples were dried at 75 °C at five different RH: 0%, 25%, 50%, 75% and 95%. EMC at 20 °C and RH 65%, impact strength, MOE and MOR, swelling and ASE were then tested and compared. Based on the results, EMC differed at 160 °C modification but not at 170 °C modification. Other properties had no significant difference between the different drying. Accessibility of hydroxyl groups was measured with DVS from the 160 °C samples dried at 50% and 95% since they had the greatest difference in EMC values. Accessibility was found to have significant differences, and therefore, it was concluded that a difference in hornification is possible between these two dryings.

Chemical analysis was carried out for unmodified sample, sample thermally modified at 170 °C and for the condensation water from the high-pressure reactor. HPAEC and GC-MS were used to analyse condensation water and the acetone soluble compounds from modified and unmodified samples. Condensation water contained many sugars from hemicelluloses, mostly mannose and xylose. It also had greatest quantity of different degradation compounds and extractives seen from GC-MS test. The acetone soluble compounds from modified and unmodified sample had some similarities, but modified sample had 38% more compounds than unmodified sample. Condensation water had hardly any similarities with the acetone soluble compounds of unmodified sample. However, modified sample and condensation water shared quite many degradation compounds as well as extractives. Based on the chemical analyses, modified samples

should be extracted before performing any tests since the number of extractives and degradation products is significant, and those may vary the results.

Based on the experiment, indication of hornification was found in thermally modified wood and the relative humidity of initial drying was assumed to have impact on the extent of hornification. However, the indication of hornification was seen only in the values of EMC at 20 °C and RH 65% with 160 °C modification. Mechanical tests and swelling test had no statistical difference between the different assumed states of hornification in this experiment. In order to be sure of this result, additional tests should be performed. The impact of extractives should be ruled out and the initial drying should be performed with more reliable equipment. Also, initial drying should be performed to material from the same thermal modification patch to rule out the effect of different modification. The accessibility of hydroxyl groups should be measured multiple times, and the extent of hornification in the sample should be analysed based on that measurement and not assumed from EMC as was done in this experiment.

Even though this experiment showed that the presumed hornification had no significant impact on the properties of thermally modified Scots pine under saturated steam, hornification is a phenomenon that should be understood better in the field of solid wood. There was at least indication that hornification might influence the EMC in thermally modified wood which is essential also for some other properties that were not measured in this thesis, such as biological resistance. All in all, the properties and the potential of thermally modified wood under saturated pressure are still poorly understood and more research is needed in every respect.

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APPENDIX 1 – MECHANICAL RESULTS IN FIGURES

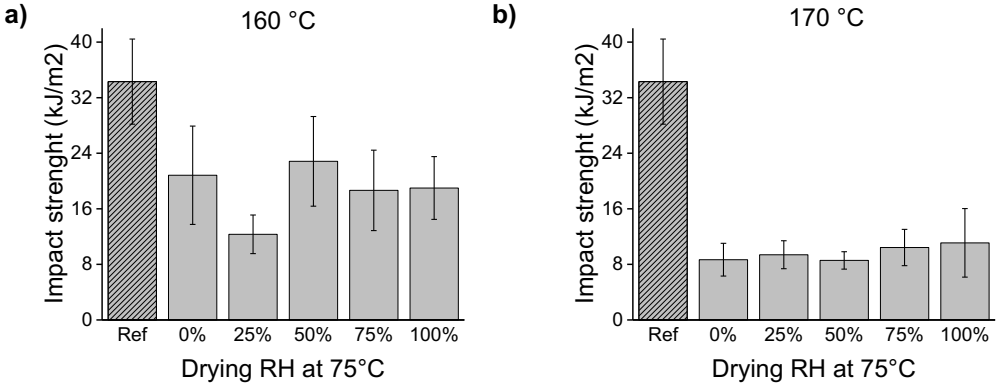

Figure 32: *Charpy impact test results for samples thermally modified at* ***a)*** *160 °C* ***b)*** *170 °C.*

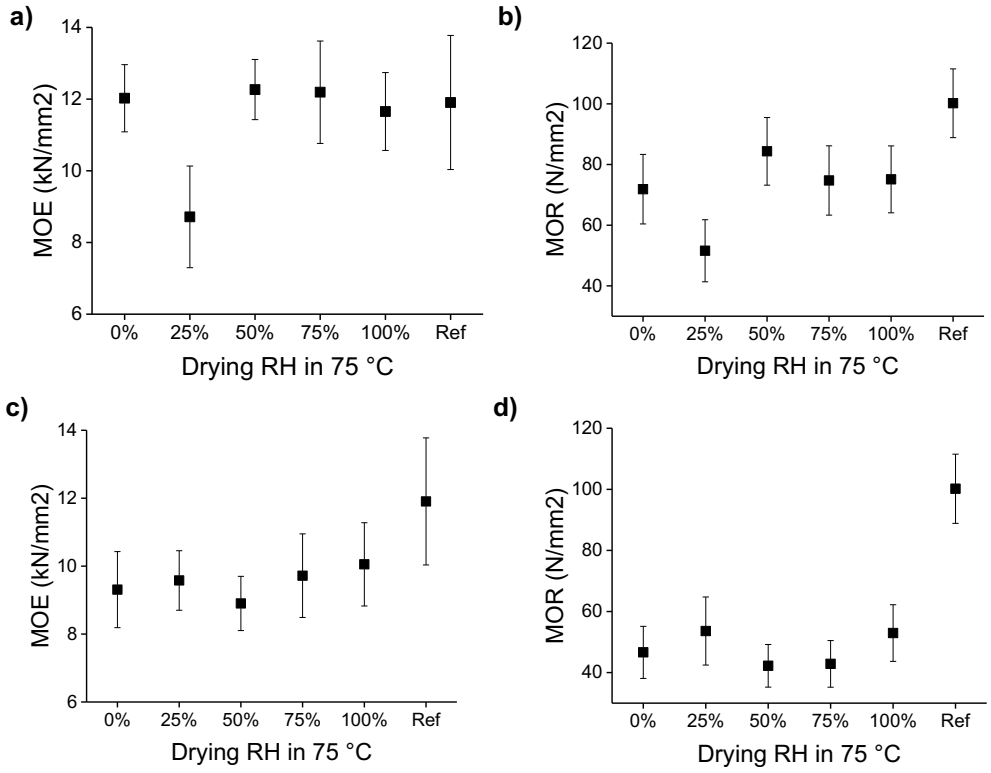

Figure 33: a) *MOE* ***b)*** *MOR for samples thermally modified in 160 °C.* ***c)*** *MOE* ***d)*** *MOR for samples thermally modified in 170 °C.*

APPENDIX 2 – SWELLING TEST RESULTS IN FIGURES

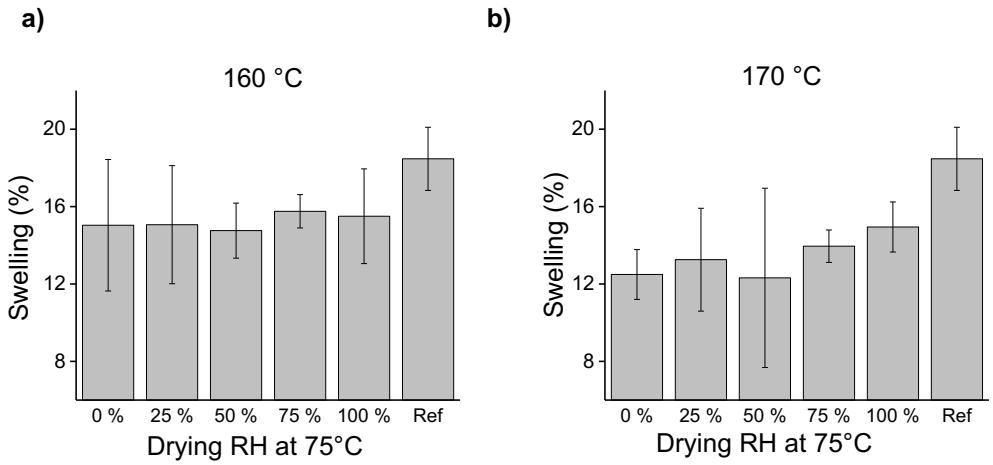

***Figure 34**: Swelling results for thermally modified samples at **a)** 160 °C **b)** 170 °C.*

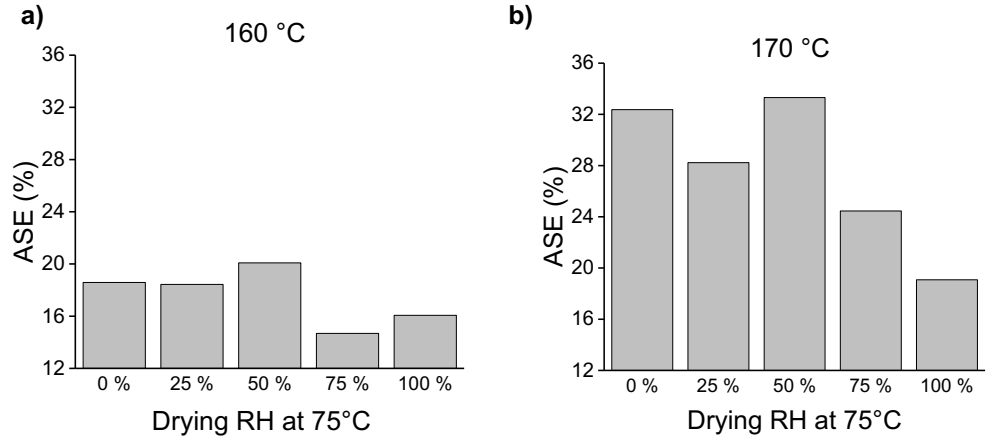

***Figure 35:** ASE results for thermally modifies samples at **a)** 160 °C **b)** 170 °C*

APPENDIX 3 – ANOVA ANALYSIS FOR 160 °C

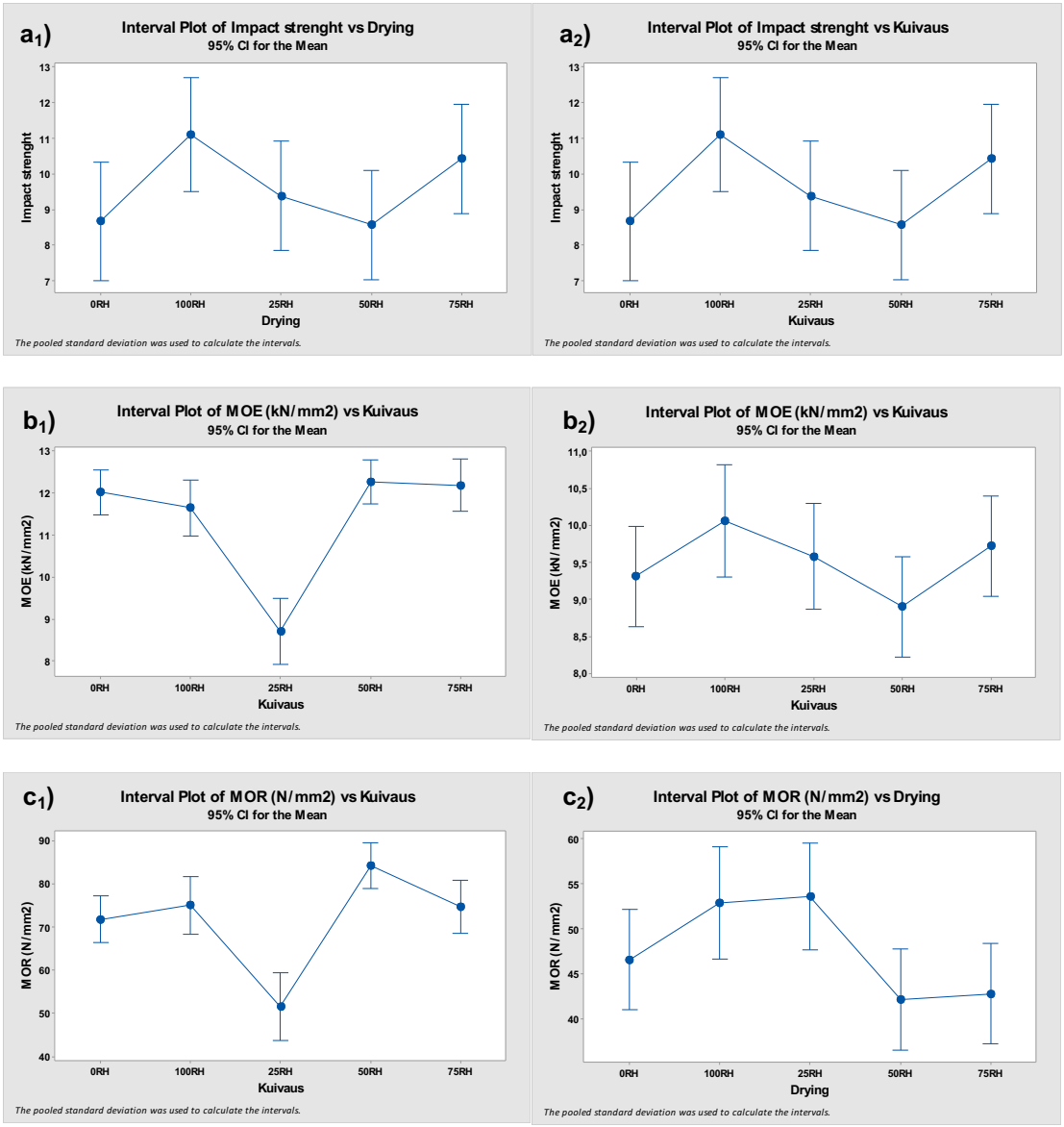

Figure 36: *ANOVA analysis for* ***a)*** *the impact test results* ***b)*** *MOE results and* ***c)*** *MOR results. In the left are the samples thermally modified in 160 °C and in the left thermally modified in 170 °C.*

APPENDIX 4 – GC-MS ANALYSIS RESULTS

Table 5: *Results from MS spectra comparison to library.*

Sample	Peak in GC spectra (min)	Compound option(s)	Probability (%)
Acetone soluble compounds from unmodified pine sample	6.17	Vanillin	28.6
	6.67	D-pinitol	78.0
	7.62	Azelaic acid	32.5
	7.70	Galactopyranose	9.8
	8.22	Palmitic acid	27.0
	8.88	Bromoadamantanone	28.5
	8.91	Diphenyldioxopyridazinopyrrolopyridazine	30.7
	9.03	Eicosatrienoic acid, alpha-linolenic acid	15.3, 10.3
	9.16	9-Octadecenoic acid, petroselic acid	17.8, 13.3
	9.70	Pimaric acid	55.9
	9.89	Eicosapentaenoic acid, doconexent, abietic acid	15.3, 11.8, 9.2
	9.93	Isopimaric acid	26.6
	10.13(16)	Dehydroabietic acid	36.2
	10.27	Acetyl-cholenic acid	23.8
	10.69	Methylprednisolone, Fluorometholone	26.3, 24.3
	11.07	Estrone glucuronide	24.7
	12.19	7-Oxodehydroabietic acid, trimethylsilyl ester	18.9
	12.21	Milbemycin B	14.5
Acetone soluble compounds from thermally modified pine sample	6.12	Vanillin	50.4
	6.27	D-xylose, D-lyxopyranose,	6.6, 6.6
	6.34	D-galactopyranose	6.7
	6.55	D-mannopyranose	6.3
	6.67	Levoglucosan	20.2
	6.96	D-galactopyranose	7.5
	7.04	D-mannopyranose	6.7
	7.24	D-talopyranose	7.4
	7.70	D-glucopyranose	9.4
	7.86	D-ribonolactone	15.1
	8.52	Coniferyl aldehyde	89.0
	9.13	9-Octadecenoic acid, petroselic acid, oleic acid	24.7, 16.5, 13.0
	9.68	Pimaric acid	48.6
	9.91	Isopimaric acid	41.2
	10.11	Dehydroabietic acid	41.0
	10.26	Abietic acid	77.8
	10.99	Lactone	6.5
	12.17	7-Oxodehydroabietic acid, trimethylsilyl ester	15.8
	12.69	4-Estren-3,17-dione, di-trimethylsilyl	21.4
Condensation water	6.18	D-xylose	30.9
	6.28	D-ribose	17.0
	6.34	Vanillin	48.7
	6.46	D-xylose	16.7
	6.76	D-allopyranose, D-mannopyranose	9.1, 6.3
	7.12	D-galactopyranose, D-talopyranose	14.9, 9.0
	7.24	D-mannopyranose	9.9
	7.38	D-talofuranose, D-allofuranose	29.8, 27.0
	7.46	D-allopyranose	8.5
	7.69	Malic acid	16.0
	7.91	D-glucopyranose	9.3
	8.81	Coniferyl aldehyde	91.4
	9.26	Gulonic acid, y-lactone	24.5
	10.46	2-Methyl-1,2-bisbutane	9.0
	11.21	D-lactose, D-cellobiose	16.0, 12.6
	11.63	Maltose	10.3
	11.78	D-lactose, D-cellobiose	15.0, 11.0
	12.03	Ambodryl, 2-trimethylsilyloxyheptanoic acid	15.1, 14.5
	12.15	Maltose	12.0
	14.61	Levulinic acid	11.4